

European
Materials Research Society
Spring Meeting

E-MRS'98

Scientific / Technical Symposia
&
Exhibition

Congress Center

- Palais de la Musique et des Congrès -
Strasbourg (France)

June 16 - 19, 1998

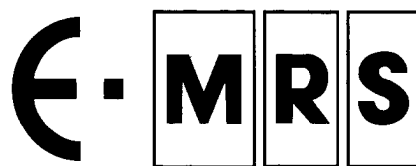


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**BOOK
of
ABSTRACTS**

€-MRS

E-MRS'98 SPRING MEETING



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June 17-18, 1998

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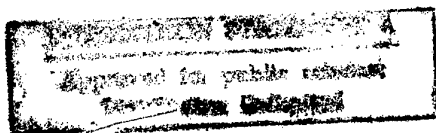
E-MRS'98 SPRING MEETING



**EUROPEAN
MATERIALS RESEARCH SOCIETY
1998
SPRING MEETING**

**June 16-19, 1998
Congress Center
- Palais de la Musique et des Congrès -
STRASBOURG (France)**

FINAL BOOK OF ABSTRACTS



E-MRS 98 Spring Meeting Conference Chairmen:

- | | | | |
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19990202 041

PLENARY SESSION

Wednesday June 17, 1998

Mercredi 17 juin 1998

Morning

Matin

| | | |
|-------------|-------------|---|
| PS-1 | 8:30-9:05 | S. NAKAMURA Nichia Chemical Industries Ltd., Anan, Tokushima 774-8601, Japan «PRESENT AND FUTURE OF GaN-BASED BLUE/GREEN LEDs» |
| PS-2 | 9:05-9:40 | M. ERMAN Director of Optical Systems Department, ALCATEL, Route de Nozay, 91460 Marcoussis, France «OPTOELECTRONIC DEVICES FOR FUTURE TELECOMMUNICATION SYSTEMS» |
| PS-3 | 9:40-10:15 | G. ABSTREITER Walter Schottky Institut, Technische Universität München, Am Coulomb-Wall, 85748 Garching/München, Germany «SEMICONDUCTOR-NANOSTRUCTURES, BASICS AND POSSIBLE APPLICATIONS» |
| PS-4 | 10:15-10:50 | D.J. EHRLICH Whitehead Institute, Massachusetts Institute of Technology, Nine Cambridge Center, Cambridge MA 02142, USA «BIOMEMS: MICRODEVICES FOR THE BIOMOLECULAR INFORMATION AGE» |
| | 10:50-11:10 | BREAK |
| PS-5 | 11:10-11:45 | U. SCAPANINI President of the Committee on Research, Technological Development and Energy of the European Parliament |
| PS-6 | 11:45-12:20 | Dr. FORSTER Commission of the European Communities, ESPRIT, Brussels, Belgium |
| PS-7 | 12:20-12:55 | Dr. GRIES Bundesministeriums für Bildung, Wissenschaft, Forschung und Technologie, Bonn, Germany |
| | 12:55 | LUNCH |

E-MRS'98 SPRING MEETING



| | |
|--------------------|--|
| SYMPOSIUM A | Defects in Silicon: Hydrogen |
| SYMPOSIUM B | Light Emission from Silicon: Progress Towards Si-based Optoelectronics |
| SYMPOSIUM C | Growth, Characterization and Applications of Bulk II-VI's |
| SYMPOSIUM D | Thin Films Epitaxial Growth and Nanostructures |
| SYMPOSIUM E | Thin Films Material for large Area Electronics |
| SYMPOSIUM F | Technique and Challenges for 300mm Silicon: Processing, Characterization, Modelling and Equipments |
| SYMPOSIUM G | Surface Processing: Laser, Lamp, Plasma |
| SYMPOSIUM H | Materials Aspects in Microsystem Technologies |
| SYMPOSIUM I | Rapid Thermal Processing |
| SYMPOSIUM J | Ion Implantation into Semiconductors, Oxides and Ceramics |
| SYMPOSIUM K | Carbon-based Materials for Microelectronics |
| SYMPOSIUM L | Nitrides and Related Wide Band Gap Materials |
| SYMPOSIUM M | Molecular Photonics for Optical Telecommunications: Materials, Physics and Device Technology |
| SYMPOSIUM N | Material and Processes for Submicron Technologies |

E-MRS'98 SPRING MEETING



SYMPOSIUM A

Defects in Silicon: Hydrogen

Symposium Organizers

- J. WEBER** Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany
- A. MESLI** CNRS/PHASE, Strasbourg, France

The assistance provided by
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SYMPOSIUM A

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - H₂ Molecules in Silicon, Part 1

Chairperson: M. Stavola, Lehigh University, Bethlehem, USA

- A-I.1** 8:30-9:05 - Invited - **H₂ MOLECULES IN CRYSTALLINE SILICON, R.E. Pritchard, M.J. Ashwin, R.C. Newman and J.H. Tucker, IRC for Semiconductor Materials, Imperial College, London SW7 2BZ, UK**
- Infrared absorption spectra from lightly-doped, hydrogenated CZ Si show weak vibrational modes from interstitial hydrogen molecules. Two of these modes arise from molecules paired with O_i atoms (O_i - H₂ centres), as confirmed by the detection of a correlated oxygen mode. The other H₂ mode is detected at 3618 cm⁻¹ and has been labelled ν_{3HH} . Annealing (T < 200°C) produces reversible, anti-correlated changes in the equilibrium concentrations of O_i-H₂ and ν_{3HH} , allowing a determination of the number density of sites accessible to a H₂ molecule in the latter location. This number is between 10²² - 10²³ cm⁻³ and we therefore identify ν_{3HH} with the mode of an isolated molecule at a tetrahedral lattice site. The dipole moment per unit displacement is estimated to be $\eta \sim 0.1e$ and the H₂ alignment must be either <111> or <110> to account for the infrared activity. The ν_{3HH} mode is also detected in hydrogenated boron-doped FZ Si, together with the hydrogen vibrational mode of H - B pairs. An estimate of the isolated molecule concentration indicates that this is the source of so-called "hidden hydrogen" that is observed for boron-doped and gallium-doped Si. This identification is confirmed in the present sample by a second low temperature annealing study, that reveals irreversible, anti-correlated changes in the equilibrium concentrations of H - B pairs and isolated H₂ molecules (ν_{3HH}). Further work is in progress to understand the dissociation mechanism of H₂ molecules and the subsequent formation of H - B pairs.
- A-I.2** 9:05-9:40 - Invited - **FORMATION OF H₂ MOLECULES IN CRYSTALLINE SILICON, A.W.R. Leitch, Department of Physics, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000, South Africa; J. Weber and V. Alex, Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany**
- Raman spectroscopy has been used to measure the presence of isolated hydrogen molecules in crystalline Si, after exposure to a hydrogen plasma. It is found that whereas a higher temperature during plasma treatment results in the incorporation of the H₂ molecules within extended voids created by hydrogen induced platelets, a lower plasma temperature favours the formation of isolated H₂ molecules, positioned at the T site within the Si lattice. Recent results for both n- and p-type Si will be presented.
- A-I.3** 9:40-10:00 **FORMATION PROCESS AND SITES OF HYDROGEN MOLECULES IN CRYSTALLINE SILICON, K. Murakami, N. Fukata, K. Ishioka*, M. Kitajima*, H. Haneta** and S. Fujimura***; Institute of Materials Science, University of Tsukuba, Tennoudai 1-1-1, Tsukuba, Ibaraki 305, Japan; *National Research Institute of Metals; **National Institute for Research in inorganic Materials; ***Fujitsu Ltd.**
- We present the experimental results^{1,2)} of hydrogen molecules in crystalline silicon that are introduced by a remote hydrogen-atom-treatment (HAT), and also new results concerning the formation process and sites of hydrogen molecules. The previous studies^{1,2)} revealed that (1) hydrogen molecules are detected by Raman scattering measurement¹⁾, (2) the Raman shift is very similar with that of hydrogen gas, but the Raman width becomes two order broader than that of hydrogen gas, (3) there are two kinds of hydrogen configurations for hydrogen molecules²⁾ corresponding to the Raman shifts of 4160 and 4130 cm⁻¹, and (4) the Raman bands at 4160 and 4130 cm⁻¹ become the maximum in the intensity at the hydrogenation temperatures of 400 and 250°C, respectively.²⁾ There has been a controversial question concerning the site of hydrogen molecules; i.e. hydrogen molecules exist in T_d interstitial sites, in platelets or in multivacancies in crystalline silicon.³⁻⁵⁾ In order to answer the question, we have performed (a) a sequential treatment of hydrogen and deuterium, (b) Si ion implantation to form multivacancies, followed by HAT, (c) HAT of amorphous Si:H and microcrystalline Si:H, and (d) hydrogen ion implantation and we have carried out Raman measurements and SIMS measurements for the samples. New results obtained for these experiments will be presented.
- References:
 1) K. Murakami et al. Phys. Rev. Lett. 77, 3161 (1996)
 2) N. Fukata et al. Phys. Rev. B56, 6642 (1997)
 3) J. Vetterhöffer et al. Phys. Rev. Lett. 77, 5409 (1996)
 4) R.E. Pritchard et al. Phys. Rev. B56, 13118 (1997)
 5) Y. Okamoto et al. Phys. Rev. B56, 10016 (1997) red lattice in Si.

SYMPOSIUM A

A-I.4 10:00-10:20

EFFECTS OF CRYSTAL DISORDER ON THE MOLECULAR HYDROGEN FORMATION IN SILICON, M. Kitajima, K. Ishioka, National Research Institute for Metals, Tsukuba, 305 Japan; S. Tateishi, K. Nakanoya, N. Fukata, K. Murakami, University of Tsukuba, Tsukuba, 305 Japan, S. Fujimura, Fujitsu Ltd., Kawasaki, 211 Japan and S. Hishita, National Institute for Research in Inorganic Materials, Tsukuba, 305 Japan
We have investigated quantitatively the effect of crystal disorder on the formation of hydrogen molecule in crystalline silicon. Microcrystalline silicon with different crystalline sizes was obtained by implanting FZ p-Si(100) with 200 keV Si⁺ with doses ranging from 10¹² to 10¹⁶ Si/cm². The degree of crystal disorder of the implanted samples was estimated in terms of the phonon correlation length from the Raman spectral shape of the LO phonon line. The LO phonon line broadened and downshifted with increasing ion dose increased, corresponding to an increase in crystal disorder and decrease in phonon correlation length. The implanted samples were then treated with atomic hydrogen in a remote downstream of hydrogen plasma at 250 °C for 3h. The vibrational Raman line of hydrogen molecule at around 4160 cm⁻¹ decreased monotonically in its intensity with increasing ion dose. The results suggest that hydrogen molecules are formed preferably in well-ordered lattice in Si.

10:20-10:50

BREAK

SESSION II - H₂ Molecules in Silicon, Part 2

Chairperson: R.E. Pritchard, IRC for Semiconductor Materials, Imperial College, London, UK

A-II.1 10:50-11:20

- Invited -

ENERGETICS AND VIBRATIONAL FREQUENCIES OF INTERSTITIAL H₂ MOLECULES IN SEMICONDUCTORS, Ch.G. Van de Walle, Xerox PARC, 3333 Coyote Hill Road, Palo Alto CA 94304, USA

Hydrogen molecules are one of the more stable forms of hydrogen in semiconductors. Recently the first experimental observations of interstitial H₂ molecules were reported. To properly interpret these results a theoretical framework is essential. We have investigated the incorporation of H₂ molecules on interstitial sites using a density-functional-pseudopotential approach. Five different materials were considered: Si, GaAs, InAs, GaP, and GaN. Combined with calculations for H₂ in vacuum, these results enable us to examine trends and develop an understanding of the physics of incorporation of a strongly bound molecule in a semiconducting environment. We find that the vibrational frequency of the interstitial molecules is shifted down significantly compared to the free molecule. The results confirm a recent assignment of Raman lines to interstitial H₂ in GaAs,¹ but contradict an assignment² claiming that the frequency for H₂ in Si is close to the free-molecule value. We will correlate the significant weakening of the H-H bond with the semiconductor host charge density near the interstitial site.

¹ J. Vetterhöffer, J. Wagner, and J. Weber, Phys. Rev. Lett. 77, 5409 (1996).

² K. Murakami, N. Fukata, S. Sasaki, K. Ishioka, M. Kitajima, S. Fujimura, J. Kikuchi, and H. Haneda, Phys. Rev. Lett. 77, 3161 (1996).

A-II.2 11:20-11:40

MOLECULAR HYDROGEN TRAPS WITHIN SILICON, B. Hourahine, R. Jones, Department of Physics, The University of Exeter, Exeter, EX4 4QL, UK; S. Oberg, Department of Mathematics, University of Lulea, Lulea, 97187, Sweden; R.C. Newman, Imperial College, Prince Consort Road, London, SW7 2BZ, UK; P.R. Briddon, Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK; E. Roduner Institut für Physikalische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany

We present the results of first principle calculations on the behaviour of molecular hydrogen both as a species trapped at several distinct boron related defects within the Si lattice and also as an isolated interstitial molecule either at interstitial sites in the undamaged crystal or within voids in the material.

These results are compared with recent experimental infra-red and Raman data obtained for silicon treated by either hydrogen plasma or soaked in hydrogen gas.

A-II.3 11:45-12:05

INTERACTION OF HYDROGEN (DEUTERIUM) MOLECULES WITH INTERSTITIAL OXYGEN ATOMS IN SILICON, V.P. Markevich, M. Suezawa, Institute for Materials Research, Tohoku University, Sendai 980-77, Japan, and L.I. Murin, Institute of Solid State and Semiconductor Physics, Minsk 220072, Belarus

Formation kinetics of oxygen-hydrogen (deuterium) complexes which give rise to an infrared absorption line at 1075.1 (1076.4) cm⁻¹ have been studied with a method of isothermal annealing in the temperature range of 30-150°C in Czochralski-grown Si crystals with different oxygen content. It was found the capture of mobile hydrogen molecules (H₂) by interstitial oxygen atoms accounts for the considered formation kinetics.

The values of diffusivity of hydrogen (deuterium) molecules and binding energy of O_i-H₂ (D₂) complex were estimated from the analysis of the results obtained.

12:05-13:30

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III - Interaction of Hydrogen with defects, Part 1**Chairperson: R. Jones, The University of Exeter, UK**

- A-III.1** 13:30-14:05 - Invited - **HYDROGEN-DEFECT INTERACTIONS IN SILICON, S.K. Estreicher**, J.L. Hastings, Physics Dept., Texas Tech University, Lubbock TX 79409, USA and P.A. Fedders, Physics Dept., Washington University, St. Louis MO 63130, USA
The interactions between hydrogen and intrinsic defects in silicon have been studied using ab-initio (tight-binding) molecular-dynamics in supercells, and ab-initio Hartree-Fock in molecular clusters. The binding energies and configurations of hydrogen bound to a self-interstitial (I), a vacancy (V), or small V aggregates are calculated. Theory predicts that the V and I, both rapid diffusers in Si, efficiently dissociate interstitial H₂ molecules. At low temperatures, this dissociation results in the formation of {V, H, H} or {I, H, H} complexes. At higher temperatures, one or both H's are released as interstitials.
- A-III.2** 14:05-14:40 - Invited - **HYDROGEN TRAPPED AT INTRINSIC DEFECTS AND LIGHT IMPURITIES IN SILICON, B. Bech Nielsen** and K. Bonde Nielsen, Institute of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark
Silicon and hydrogen form strong covalent bonds. As a consequence, intrinsic defects in crystalline silicon, which possess dangling- or elongated-bonds, are effective trapping sites for hydrogen atoms. Detailed information about the resulting hydrogen defects may be obtained with structure sensitive techniques, such as FTIR, EPR, and ion channeling. Information related directly to the hydrogen atom is obtained from observation of Si-H stretch modes by FTIR spectroscopy and from the lattice sites occupied by implanted deuterons as determined from ion channeling measurements. The electronic levels within the band gap of hydrogen defects appear largely to be associated with combinations of silicon orbitals and to be only weakly affected by the hydrogen atom. Hence, EPR studies of the electronic Ground State give complementary information on the overall structure of the defects. In this presentation, we present a review of our work on H₂* and vacancy-hydrogen defects. It is argued that structure-sensitive techniques together with ab initio theory have given us a detailed understanding of these complexes at the atomic level. Finally, we shall describe our recent investigations of hydrogen-oxygen and hydrogen-carbon complexes. It is suggested that the strain field around an oxygen or a carbon impurity is responsible for the trapping of the hydrogen atom.
- A-III.3** 14:40-15:00 **VACANCY-HYDROGEN DEFECTS IN Ge AND Si-Ge, J. Coomer**, R. Jones, Department of Physics, The University of Exeter, Exeter, EX4 4QL, UK; S. Oberg, Department of Mathematics, University of Luleaa, Luleaa 97187, Sweden; P.R. Briddon, Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
It is likely that chemical vapour deposition methods used for the preparation of Si-Ge alloys lead to the formation of vacancies which can be stabilised by interacting with hydrogen. The structure and electrical levels associated with these defects in Ge, Si, and Si-Ge alloys are analysed using a density functional cluster approach and the electrical levels of the defects are found using a Slater transition state argument.
- A-III.4** 15:00-15:20 **HYDROGEN-ENHANCED OXYGEN CLUSTERING IN SILICON, L.I. Murin** and V.P. Markevich, Institute of Solid State and Semiconductor Physics, Minsk 220072, Belarus; J. Lennart Lindström and T. Hallberg, Linköping University, Department of Physics and Measurement Technology, 581 83 Linköping, Sweden
Formation of small oxygen clusters (dimers, trimers and the first species of the thermal double donors) in Czochralski-grown Si crystals pre-heat-treated at high temperature in hydrogen gas has been studied using electrical (Hall effect) and optical (IR-absorption) measurements. The presence of hydrogen is revealed to result in an enhanced diffusion rate not only for the interstitial oxygen atoms but for the oxygen dimer as well. Some indications of the effect of hydrogen on the migration ability of the oxygen trimer and the bistable thermal donors have also been found.
- 15:20-15:50 **BREAK**

SYMPOSIUM A

SESSION IV - Interaction of Hydrogen with Defects, Part 2

Chairperson: B. Bech. Nielsen, University of Aarhus, Denmark

- A-IV.1** 15:50-16:25 - Invited - **PHOTOLUMINESCENCE CHARACTERISATION OF HYDROGEN-RELATED DEFECTS IN SILICON**, **A.N. Safonov** and E.C. Lightowers, Physics department, King's College London, Strand, London WC2R 2LS, UK
Hydrogen is known to actively participate in the formation of various defect complexes during the thermal treatment of silicon. Many of them can be observed by photoluminescence (PL), which can be used for monitoring the presence of hydrogen in the material and its effect on thermal defect formation. In the present work we consider the application of PL techniques for investigating the structural and electronic characteristics of several centres which appear in silicon due to interaction of H with C, O and native defects. The combination of uniaxial stress, magnetic field and temperature-dependence measurements has been used for determining the origin of the luminescence, and the electronic properties of the defects. It has been found that the majority of systems can be successfully described in single particle or bound exciton approximation, and that they correspond to transitions between shallow- and deep-level states of the defects. In particular, it is shown that different configurations of carbon-hydrogen complexes produce a series of deep acceptor levels in the upper half of the band gap. The isotope analysis of zero-phonon lines and local vibrational modes has been carried out for several multi-hydrogen, C-H, and C-H-O centres, which allows the atomic composition of the defects to be identified.
- A-IV.2** 16:25-16:45 **THE C-TYPE DEFECT ON Si (001) AS A HYDROGEN-VACANCY COMPLEX**, **T. Miyazaki**, T. Uda*, and K. Terakura, JRCAT-NAIR, *JRCAT-ATP, Higashi 1-1-4, Tsukuba 305, Japan
Atomic and electronic structures of the C-type defect on Si(001) are studied using an ab initio method based on the density-functional theory with the spin-polarized local-density approximation. We consider a model where a H atom is captured in a mono-vacancy on the second surface layer, which is an extension of the Uda-Terakura (UT) model (Phys. Rev. B53, 6999 (1996)). Our modeling is motivated by a result that the UT's model is not stable enough against adsorption of a Si atom. We find that our H-vacancy complex model optimized has a spin gap of about 0.2eV. The spin polarization is localized at the defect, which produces a large LUMO amplitude relative to that of a clean surface. This feature appears to be consistent with bright protrusions of the C-type defect at the empty state observed with STM.
- A-IV.3** 16:45-17:05 **DIPOLAR INTERACTIONS BETWEEN UNPAIRED Si BONDS AT THE (111)Si/SiO₂ INTERFACE**, A. Stesmans and B. Nouwen, Department of Physics, University of Leuven, 3001 Leuven, Belgium
Thermal oxidation of Si gives rise to the natural generation of defects at the Si/SiO₂ interface as a result of lattice-network mismatch. In standard thermal (111)Si/SiO₂, the dominant paramagnetic defect observed by electron spin resonance (ESR) is the P_b center (interfacial •Si≡Si₃), of which, in the as grown state, a density of ~4.9x10¹² cm⁻² is inherently incorporated for the oxidation range 300-950 °C. In the present work, it was found that the P_b density may be strongly enhanced by appropriate postoxidation annealing in hydrogen ambient, up to ~3.1x10¹³ cm⁻²—the maximum density so far reported. This has opened new perspectives to studying the dipolar interaction effects within the two dimensional P_b spin system. While in previous study, restricted to P_b densities ≤1x10¹³ cm⁻², the dipolar interaction effects could only be demonstrated by monitoring the concentration dependence of the ESR parameters, the effects are now directly revealed in the magnetic field anisotropy of the line width (and shape), well distinct from the known anisotropic strain broadening. Successful quantitative simulation of the field angle dependences by a computational model has enabled profound analysis of the line broadening mechanisms, providing evidence for a concentration dependent strain broadening contribution. Additional detailed susceptibility measurements demonstrate the absence of any significant spontaneous magnetic ordering within the P_b system in the liquid-He temperature range. The results are discussed in the light of the P_b defect distribution over the interface plane.
- A-IV.4** 17:05-17:45 **IONIZATION AND TRAPPING OF HYDROGEN NEAR SiO₂ INTERFACES**, **V.V. Afanas'ev** and A. Stesmans, Department of Physics, University of Leuven, 3001 Leuven, Belgium
Annealing of structures composed of SiO₂ and (111)Si, (100)Si, (100)3C-SiC, (0001)4H-, 6H-SiC in H₂ in the temperature range 450-800°C is found to introduce a considerable density (up to 10¹³ cm⁻²) of positively charged centers in interfacial regions. The charge is eliminated by subsequent annealing in vacuum. The latter finding together with the reversibility of charging process suggest the relationship of the charge to hydrogen bonding in some state. The activation energy of dissociation of this state was found to be 2.3 - 2.4 eV. Importantly, there is no comparable density of dangling bonds initially present nor generated at the Si/SiO₂ interfaces or in the SiO₂ layer that could account for the observed hydrogen bonding. Therefore, the hydrogen is suggested to be trapped in the positively charged valence alternation state—threefold coordinated oxygen—resembling the well known hydronium ion (H₃O)⁺. The observed sensitivity of the charge to the conduction band offset at the semiconductor/SiO₂ interface and the doping type of the wide-gap SiC (4H, 6H) indicate the interface ionization of hydrogen to be involved in the rate-limiting stage of the charge generation.

A-IV.5 17:45-18:05

LOW TEMPERATURE HYDROGENATION OF DISLOCATED Si, O.V. Feklisova, E.B. Yakimov, N.A. Yarykin, IPTM RAS, Chernogolovka 142432, Russia; J. Weber, MPI-FKF, 70506 Stuttgart Germany

The passivation of dislocation related centers in n-type Si due to chemical etching and subsequent annealing is reported. Dislocations with a density of $10^6\text{--}10^7\text{cm}^{-2}$ were introduced by four-point bending at 625°C . After the deformation the samples were chemically etched in a mixture of HF and HNO_3 acids. Some samples were subsequently annealed at $100\text{--}300^\circ\text{C}$ for 30 minutes. Finally, Schottky diodes were prepared by gold evaporation. The DLTS measurements show that in all the samples the well-known B and D dislocation-related centers with activation energies at 0.29 and 0.56 eV are dominant. After chemical etching the depth profiles of these defects are flat and there is no indication of passivation. Only annealing at temperatures higher than 300°C results in a significant decrease of both B and D centers in the near surface region. To check the hydrogen penetration into the samples, the dislocated samples were irradiated with 5 MeV electrons resulting in the formation of radiation defects. Just after etching and more pronounced after annealing at $100\text{--}150^\circ\text{C}$ we find a noticeable passivation of the radiation defects in these samples but no changes in the dislocation center concentration. This indicates that an additional thermal excitation is needed to activate the hydrogen-dislocation center reaction. A quantitative analysis of the defect depth profiles is given.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION V - Hydrogen in processing

Chairperson: K. Bond Nielsen, University of Aarhus, Denmark

- A-V.1** 13:30-14:05 Invited **SURFACE DOPANT CONCENTRATION MEASUREMENT USING THE SURFACE CHARGE PROFILER METHOD (SCP) : CHARACTERIZATION OF HYDROGEN AND METALLIC CONTAMINATION IN SILICON**, A. Danel, F. Tardif, Gressi-Leti-CEA/G, 38054 Grenoble Cedex 9, France, and G. Kamarinos, ENSERG, LPCS, BP 257, 38016 Grenoble Cedex 1, France
The change of the active doping concentration in the near surface region of silicon wafers is measured accurately using non contact SCP. The direct hydrogen contamination from different chemistries used in industrial cleanings is studied as well as doping modification induced by metals.
In p-type wafers, boron deactivation by pairing with contaminants is responsible of doping changes. Activation energies of pairs formed during various processes are here measured using SCP and thermal reactivation. This paper reports that metallic contaminations are not directly involved in doping shift but enhance hydrogen contamination. Thus, purity of HP chemistries is monitored by measurement of active doping after cleaning.
- A-V.2** 14:05-14:25 **HYDROGEN ENHANCEMENT OF THERMALLY INDUCED INTERFACE DEGRADATION IN THERMAL Si/SiO₂ TRACED BY ELECTRON SPIN RESONANCE**, A. Stesmans and V.V. Afanas'ev, Department of Physics, University of Leuven, 3001 Leuven, Belgium
Recently, the process of thermal interface degradation induced in thermally grown (111)Si/SiO₂ during post-oxidation annealing (POA) in vacuum was identified by electron spin resonance as distinct creation of persistent P_b (•Si≡Si₃) interface defects, in addition to the inherent density of ~4.9x10¹²cm⁻² initially present in the as-oxidized state. The degradation is observed from an anneal temperature of ~640°C onward as intense creation of P_bs in densities N_c monotonically increasing with anneal temperature with no trend toward saturation up to ~1200°C, where N_c ~1.3x10¹³cm⁻². In the present work, it was observed that hydrogen ambient strongly enhances (~6 times) the degradation effect, the process now initiating from ~550°C onward. It thus appears that POA in hydrogen containing ambient, often used to passivate preexisting interface states inherently introduced during oxidation, effectively creates extra defect entities, which then have to be passivated additionally. It shows that the POA ambient, i.e., vacuum *vis-B-vis* hydrogen, plays a key role in interface degradation. The data reveal the atomic nature of one of the mechanisms of the electrically long known hydrogen-induced POA generation of adverse interface defects.
- A-V.3** 14:25-14:45 **INFLUENCE OF HYDROGEN DESORPTION ON THE GENERATION OF DEFECTS IN LEPECVD**, C. Rosenblad, H.R. Deller, H. von Känel, ETH Zürich, 8093 Zürich, Switzerland and P. Schroeter, Neu-Technikum Buchs, 9471 Buchs, Switzerland
Adsorbed hydrogen on the surface has been shown to affect the thickness to which the Si film can be grown epitaxially. In our system for "low energy DC-plasma enhanced chemical vapor deposition" (LEPECVD), the growing film is exposed to an intense but low voltage plasma discharge. We have studied the effect of adsorbed hydrogen on the crystal quality of epitaxial Si films by cross-sectional transmission electron microscopy. These studies show that, for growth rates exceeding a certain threshold, adsorbed hydrogen leads to the nucleation of stacking faults after a certain thickness of epitaxial growth. The defects can be avoided by increasing the hydrogen desorption either by increasing the plasma intensity or by mixing small amounts of Ge into the film, hence using the smaller binding energy of Ge-H compared to Si-H. At the highest plasma density achievable, epitaxial silicon is obtained at substrate temperatures down to 500°C and at growth rates exceeding 1 nm/s.
- A-V.4** 14:45-15:15 **HYDROGEN PASSIVATION OF NEWLY DEVELOPED EMC-MULTI-CRYSTALLINE SILICON**, R. Einhaus, F. Duerinckx, E. Van Kerschaver, J. Szlufcik, IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium; F. Durand, P.J. Ribeyron, J.C. Duby, EPM-MADYLAM, BP 95, 38402 St-Martin d'Heres, France; D. Sarti, G. Goar, G.N. Le, PHOTOWATT, 38402 Bourgoin Jallieu, France; S. Martinuzzi, J.F. Gatto, I. Périchaud, LPDSO, Case 231, 13397 Marseille, France
Continuous casting with an electromagnetic cold crucible is a promising way of producing multi-crystalline(mc) silicon on an industrial basis for solar cell production. Casting equipment, capable of producing ingots of 130x130 mm² cross-section and 600 mm length has been developed and installed. Thorough characterisation of the produced material shows for the present mc wafers a relatively high defect density (grain boundaries, dislocations) and small grain sizes of 1-4 mm in diameter. Optimisation of the crystallisation conditions is under way. Although the effective minority carrier diffusion length is high on as-cut wafers (>150µm) it decreases during solar cell processing to values of 50µm. This can be attributed to standard high temperature processing steps that lead to an agglomeration of residual impurities (eg. metals, carbon) along crystal defects and act as strong recombination centres. In order to passivate these recombination centres, a PECVD SiN_x-layer is deposited which acts as a source of hydrogen and also as an anti-reflective coating. During the firing of the screen-printed metal contacts through the SiN_x-layer, atomic hydrogen is released from this layer and diffuses into the bulk of the wafers where it saturates dangling bonds and passivates impurities at crystal defects. After this treatment the minority carrier diffusion length can be restored to values of around 100µm on finished solar cells.

SYMPOSIUM A

A-V.5 15:05-15:25

HYDROGEN PASSIVATION OF MULTICRYSTALLINE SILICON SOLAR CELLS, R. Lüdemann, Fraunhofer Institute for Solar Energy Systems, Oltmannsstr. 22, 79100 Freiburg, Germany

Hydrogen passivation (HP) takes advantage of the ability of hydrogen to deactivate impurities and defects in silicon, and to passivate grain boundaries. Especially multicrystalline silicon (mc-Si) for photovoltaic devices suffers from low minority charge carrier lifetimes due to the call for cost-effective and thus low-quality material.

Three kinds of hydrogen incorporation into mc-Si solar cells were evaluated: hydrogen diffusion out of a SiN-layer (SiN:H), low-energy hydrogen ion implantation (HII), and remote plasma hydrogen passivation (RPHP). Best results were obtained by RPHP, whereas using a Kaufman ion source damage exceeded the passivation effect to some extent. Different diffusion mechanisms could be found, since SiN:H passivates more the grains, while RPHP acts particular on grain boundaries.

We have investigated the influence of HP to various mc-Si materials by solar cell and lifetime measurements. CVD layers and ribbon material show the strongest increase in performance. A boost of up to 77.0 mV in the open-circuit voltage and 2.0% in the efficiency of solar cells has been achieved. Electromagnetically casted Si has shown an improvement of 2.1% in efficiency after RPHP treatment. But even mc-Si of higher quality, like mc-Baysix and Eurosolare mc-Si could be rectified by HP. Applying a standard cell process for material assessment efficiencies of 16.3 % have been realised, while 16.7% have been obtained including a RPHP step. Thus the potential for high-efficiency mc-Si solar cells is shown.

A-V.6 15:25-15:45

DOPING OF CRYSTALLINE N-SILICON WITH HYDROGEN BY AN ELECTRO-CHEMICAL METHOD, A. Robles, D. Vega, J.R. Ares, P. Martin, J.F. Fernandez and C. Sanchez, Dpto. Fisica de Materiales, Facultad de Ciencias, Universidad Autonoma de Madrid, Cantoblanco 28049 Madrid, Spain

Hydrogen doping of crystalline n-type silicon (phosphorous doped) has been achieved by means of an electrochemical method. Crystalline n-silicon samples were charged with hydrogen from a H_3PO_4 electrolyte at temperatures around 200°C. The presence of hydrogen inside the sample was investigated by several techniques: Infrared Spectroscopy, Thermal Desorption Spectroscopy (TDS) and Thermoelectric Power. Scanning Electron Microscope and X-rays Diffraction were also used in order to characterise the effect of the H-treatment on the microstructure of the n-silicon samples.

TDS has shown a H_2 desorption peak around 600 K. Hydrogen vibrations bands appear in the IR spectra. An increase on thermoelectric power from undoped to H-doped silicon samples has been measured. This change has been interpreted as due to hydrogen charge neutralisation. SEM and XRD data indicate that surface damage is introduced in the n-silicon. A clear broadening of the diffraction peaks have been observed. Discussion on the role played by H on silicon and comparison with other techniques used to doped Si with H will be presented. (Supported by DGICYT, PB96-0084).

A-V.7 15:45-16:05

HYDROGEN REDISTRIBUTION AND ENHANCED THERMAL DONOR FORMATION AT POST-IMPLANTATION ANNEALING OF P-TYPE HYDROGEN IMPLANTED CZOCHRALSKI SILICON, A.G. Ulyashin, A.I. Ivanov, I.A. Khorunzhii, Device Performance Department, Belarussian State Polytechnical Academy, Skariny Ave. 65, 220027, Minsk, Belarus and R. Job, W.R. Fahrner, Department of Electrical Engineering, University of Hagen, Haldener Str.182, 58084 Hagen, Germany and F.F. Komarov, A.C. Kamyshan, Department of Physical Electronics, Belarussian State University, Kurchatova 4, 220064, Minsk, Belarus

The hydrogen redistribution and the enhanced conversion of the region near the surface of hydrogen implanted p-type Czochralski (CZ) silicon into n-type by thermal donor (TD) formation at low-temperature (450 C) post-implantation annealing have been investigated. For comparison the low-temperature HF hydrogen plasma treated CZ Si with subsequent annealings at 450 C was investigated, too. Spreading resistance probe analysis and secondary ion mass spectroscopy were used for the samples characterization. It is shown that the hydrogen redistribution and hydrogen enhanced thermal donor (TD) formation in hydrogen implanted or plasma treated p-type CZ-Si leads to the formation of deep p-n junctions (up to a few hundred microns) after 450 C annealing. The depth of p-n junction depends on the annealing time and on the hydrogenation method. From the experiments it can be seen that the buried defect layer in hydrogen implanted CZ-Si samples acts as an effective getter for hydrogen and therefore a delay in deep p-n junction formation was observed as compared to hydrogen plasma treated samples after 450 C annealings. This delay time (of about 1.5h) characterizes the annealing time of defects in buried layer by which the hydrogen atoms are captured. The observed changes of the resistivity after post-implantation and post-hydrogen plasma treatment annealings can be explained by a hydrogen redistribution and a hydrogen enhanced thermal donor formation processes. The kinetic model for the simulation of these processes is presented.

A-V.8 16:05-16:25

PROCESSES LEADING TO DELAMINATION OF THIN LAYERS IN HYDROGEN IRRADIATED SILICON, V.P. Popov, V.F. Stas, Institute of Semiconductor Physics, Novosibirsk, Russia

The renewing interest of silicon irradiated with hydrogen ions has its background in application of this material in the technology of production of silicon-on-insulator structures, generally referred to as the "smart cut". The present work deals mainly with investigation of electrophysical characteristics of irradiated silicon. It is demonstrated that under annealing in the temperature interval 380-500°C the concentration of holes (p-type conductivity silicon) sharply decreases at depths significantly exceeding the extent of the irradiated region (up to 360-500 µm). On the basis of new results and available literature data a scheme of processes leading to delamination of thin layers of silicon is suggested. The primary role is ascribed to mobile point defects - vacancies, hydrogen atoms and self-interstitial atoms. The essence of processes is as follows: mobile hydrogen and self-interstitial atoms of silicon, appearing under annealing, interact with impurity (hydrogen) - vacancy formations, which leads to an increase of the gas (hydrogen) pressure above the critical value and to development of cracks. Under continuous supply of hydrogen and interstitial silicon atoms the pressure in the vacancy-gas admixture is kept at the critical level and the crack propagates through the crystal.

16:25-17:05

BREAK

POSTER SESSION

17:05-18:00

See programme of this poster session p. A-13 to A-14.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning
Matin

SESSION VI: Transition-Metal-Hydrogen Complexes, Part 1

Chairperson: Ch.G. Van de Walle, Xerox Parc, Palo Alto, USA

- A-VI.1** 8:30-9:05 - Invited - **THEORY OF TRANSITION METAL HYDROGEN COMPLEXES IN SILICON**, R. Jones, A. Resende, Department of Physics, The University of Exeter, Exeter, EX4 4QL, UK; S. Oberg, Department of Mathematics, University of Luleaa, Luleaa, 97187, Sweden; P.R. Briddon, Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
The interaction of hydrogen with transition metal impurities in silicon is explored using spin-polarised local density functional cluster theory. The electrical levels of various combinations of TM-Hn defects can be understood through a displacement and splitting of the gap t_2 manifold of states due to the impurity. The calculated levels for Au-Hn and Ag-Hn defects for $n=1$ are in fair agreement with experimental values deduced by capacitance measurements. Passive complexes of these impurities are identified with $n=3$.
- A-VI.2** 9:05-9:40 - Invited - **STRUCTURE SENSITIVE SPECTROSCOPY OF TRANSITION-METAL-HYDROGEN COMPLEXES IN SILICON**, M. Stavola, M.J. Evans, M.G. Weinstein, S.J. Uffring and G.D. Watkins, Physics Department, Lehigh University, Bethlehem, PA 18015, USA
There has been much progress made toward understanding hydrogen-passivated shallow impurities in semiconductors. However, the structures and electrical properties of hydrogenated deep-level impurities have remained poorly understood. During the past few years, the introduction of hydrogen into Si at elevated temperature has permitted samples to be fabricated with a sufficient number of hydrogenated transition metal impurities to be studied by electron paramagnetic resonance and infrared absorption spectroscopies and for significant progress to be made. Several defect complexes that involve Pt or Au and H have been identified. EPR and vibrational spectroscopies provide detailed structural information and models have been proposed. It has also been possible to estimate the level positions of these defects so that their spectroscopic signatures can be related to recent DLTS results. In this talk, a survey of what has been learned from these spectroscopic studies and of unresolved issues will be presented.
* Supported by NSF Grant No. DMR-9415404
- A-VI.3** 9:40-10:00 **GOLD-HYDROGEN COMPLEXES IN SILICON**, L. Rubaldo, A.R. Peaker, D.K. Maude and J-C. Portal, Laboratoire des Champs Magnétiques Intenses MPI-CNRS, 25, ave des Martyrs, Grenoble 38042 France; P. Deixler, I.D. Hawkins and J.H. Evans-Freeman, University of Manchester, Institute of Science and Technology, Manchester M60 1QD, UK; L. Dobaczewski, Institute of Physics, Aleja Lotnikow 32/46, 02-668 Warsaw, Poland
Hole and electron emission from gold and gold-hydrogen complexes in silicon have been studied using high resolution (Laplace) DLTS. This technique permits a clear separation of defects which have very similar carrier emission characteristics. Hydrogen has been introduced into gold diffused silicon by wet etching. In n-type material both hole and electron transitions have been examined, in p-type material only hole transitions have been studied. At low hydrogen concentrations our results confirm those inferred previously from conventional DLTS. However by using 'Laplace' DLTS it has been possible to study the gold acceptor and G4 defect independently. As a result we have been able to measure the electron capture cross-section of G4 and the concentration profile of this defect. We conclude from the cross sections that G4 is acceptor like. At high hydrogen concentrations it is clear from the 'Laplace' spectra that numerous complexes are formed including a family of defects with emission characteristics similar to G1. We have preliminary evidence of meta-stability and recombination enhanced dissociation in relation to these complexes.
- A-VI.4** 10:00-10:20 **DLTS ANALYSIS OF NICKEL-HYDROGEN COMPLEX DEFECTS IN SILICON**, M. Shiraiishi*, ***, J.-U. Sachse*, H. Lemke** and J. Weber*, *Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, 70506 Stuttgart, Germany, **TU Berlin, Institut für Werkstoffe der Elektrotechnik, Jebensstraße 1, 1063 Berlin, Germany, ***SONY Corporation Research Center, 174 Fujitsuka-cho, Hodogaya-ku, 240 Yokohama, Japan
The result of a Deep Level Transient Spectroscopy (DLTS) study of nickel-hydrogen complexes in p- and n-type silicon will be presented. Ni is incorporated during the crystal growth of Si and its doping concentration is $4 \times 10^{13} \text{cm}^{-3}$. Wet-chemical etching introduces hydrogen in the samples and new levels (4 hole traps, $E_v + 0.30, 0.40, 0.51$ and 0.58eV and 2 electron traps, $E_c - 0.16$ and 0.57eV) are observed. The depth profiles of the Ni-H complexes are determined and the number of H's in the complexes is estimated from depth profiling. A hole trap of $E_v - 0.57 \text{eV}$ is interpreted as a complex containing Ni and a single H. The other traps are believed to contain two to four H's. After thermal anneals at $400 - 470 \text{K}$ for 1 hour, the DLTS lines associated with isolated Ni and all the Ni-H complexes decrease while new lines appear. We will propose possible structures for the various complexes.
- 10:20-10:50 **BREAK**

SYMPOSIUM A

SESSION VII: Transition-Metal-Hydrogen Complexes, Part 2

Chairperson: S.K. Estreicher, Texas Tech University, Lubbock, USA

A-VII.1 10:50-11:25 - Invited -

SIMILARITIES IN THE ELECTRICAL PROPERTIES OF TRANSITION-METAL HYDROGEN COMPLEXES, J.-U. Sachse, E.Ö. Sveinbjörnsson*, N. Yarykin** and J. Weber, Max-Planck-Institut f. Festkörperforschung, 70569 Stuttgart, Germany; *Department of Microelectronics ED, Chalmers University of Technology, 41296 Göteborg, Sweden; **Institute of Microelectronics Technology RAS, 142432 Chernogolovka, Russia

We will review our recent studies on the reactions of hydrogen with transition-metals TM (TM = Pd, Pt, Ag and Au) in crystalline Si. Hydrogen was incorporated into the samples by wet chemical etching. Deep-level transient spectroscopy (DLTS) on Schottky diodes reveals several TM-H complexes in n- and p-type samples. From DLTS profiling, we are able to estimate the number i of hydrogen atoms in the TM-H _{i} complexes. All complexes with $i = 1$ to 3 are electrically active with at least one or two levels in the gap. Striking similarities are found for the isoelectronic complexes, e.g. Pt-H₂ and Au-H₁. Transition metal complexes with more than 3 hydrogen atoms are likely to be electrically passive and can be detected only in regions with high hydrogen concentration. Annealing at temperatures up to 400-500K favors the formation of hydrogen rich defects. All hydrogen complexes disappear after heat treatments at 400°C for several hours. In essence, we find that the passivation of metal impurity levels by hydrogen is not a practical solution to eliminate inadvertent recombination centers in Si.

A-VII.2 11:25-12:05

HYDROGEN-RHODIUM COMPLEXES IN SILICON, J. Weber, S. Knack, Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, 70506 Stuttgart, Germany; H. Lemke, TU Berlin, Institut für Werkstoffe der Elektrotechnik, Jebensstraße 1, 1063 Berlin, Germany

Rhodium was incorporated in n-type and p-type Silicon during the floating-zone process in concentrations of 10^{13}cm^{-3} . Schottky diodes were prepared directly after cleavage without any prior chemical treatment. Only two electrical levels at $E_c - 0.59\text{ eV}$ and $E_c - 0.34\text{ eV}$ were detected in these samples by DLTS. From the homogeneous distribution of the two levels in the samples, we attribute the levels to the substitutional defect configuration of Rh. Hydrogen incorporation by wet chemical etching in a CP6 solution (HF, HNO₃, CH₃COOH) prior to the forming of the Schottky contacts introduces at least three new electronic levels.

We identify the levels with hydrogen related Rh centers containing different numbers of hydrogen atoms. The thermal stability of these complexes was investigated and similarities to the hydrogen complex formation in Co-doped Silicon samples [1,2] are reported.

[1] W. Jost, J. Weber and H. Lemke, Semicond. Sci. Technol. **11** (1996) 22-26.

[2] W. Jost, J. Weber and H. Lemke, Semicond. Sci. Technol. **11** (1996) 525-530.

A-VII.3 11:45-12:05

A FIRST PRINCIPLE STUDY OF TRANSITION METAL HYDROGEN COMPLEXES IN SILICON, A. Resende, R. Jones, Department of Physics, The University of Exeter, Exeter EX4 4QL, UK; S. Oberg, Department of Mathematics, University of Luleå, Luleå, 97187, Sweden; P.R. Briddon, Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

The interaction of hydrogen with transition metal impurities to form complexes with distinct electrical levels is investigated. A first-principles spin-polarised local density functional cluster method is used to explore the structural, electrical and vibrational properties of the complexes, and Slater's transition argument is used to derive the electrical levels of the centres. Results are given for Ni-, Pt- and Co- hydrogen complexes. The electrical levels are compared with transient capacitance measurements.

12:05-13:30

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION VIII - Alternative passivation mechanisms

Chairperson: A.N. Safonov, King's College London, UK

- A-VIII.1** 13:30-14:05 - Invited - **ELECTRICAL CHARACTERIZATION OF DEFECT REACTIONS IN SILICON: THE CASE OF COPPER, T. Heiser, A.A. Istratov,* C. Flink* and E.R. Weber,** University Louis Pasteur, Laboratoire de Physique et Applications des Semiconducteurs, CNRS, BP 20, 67037 Strasbourg Cedex 2, France, *Department of Material Science and Mineral Engineering, University of California at Berkeley, California 94720, USA
Electrical characterization of defect reactions involving interstitial copper impurities (Cu_i) in silicon are reviewed. Deep level transient spectroscopy analyses on copper-metal impurities are described and the metastable behavior of several related deep levels are discussed. Information about acceptor-copper pairing kinetics extracted from low temperature Cu_i drift experiments using capacitance voltage measurements are analyzed and the consequences on the low temperature copper diffusivity are emphasized.
Room temperature transient capacitance signals observed in copper in-diffused and quenched p-type silicon are reported and attributed to Cu_i drift. A theoretical model is developed which describes the major properties of such transient ion drift (TID) induced signals. It is found that the voltage dependence of the capacitance transients ascertains the ion-drift related nature of the signals. The similar dependence of the diffusing defect concentration and the copper solubility on the annealing temperature identifies the diffusing ion as Cu_i . Special emphasis is put on the influence of acceptor-donor pairing on the room temperature Cu_i mobility. In the case of gallium, aluminum or indium doped silicon the acceptor-copper binding energy is so large that only a pairing limited effective diffusion coefficient can be estimated. However in variously B-doped silicon and at high enough temperatures, the ion drift becomes the dominating process and enables a quantitative estimation of the Cu_i migration enthalpy. The results are compared to theoretical predictions and to previously reported diffusion data. Finally, the precipitation behavior of Cu_i at moderate temperatures are investigated using TID analyses.
- A-VIII.2** 14:05-14:25 **COPPER-RELATED COMPLEXES IN SILICON, S.K. Estreicher,** Physics Department, Texas Tech University, Lubbock, TX 79409, USA
Hartree-Fock calculations involving Cu in silicon provide insights on the interactions between (a) Cu and vacancy-related defects, (b) Cu and shallow acceptors, (c) interstitial Cu and substitutional Cu, and (d) a pair of Cu in a hexavacancy. Preliminary results include a number of relaxed configurations, chemical details of the Cu-Si interactions, and binding energies.
- A-VIII.3** 14:25-14:45 **CADMIUM-LITHIUM DEFECTS IN SILICON, C.A. Frehill, M.O. Henry, E. McGlynn,** School of Physical Sciences, Dublin City University, Collins Avenue, Dublin 9, Ireland and E.C. Lightowers, A. Safanov, Department of Physics, Kings College, Strand, London WC2R 2LS, UK
Cd and Li impurities in silicon produce a variety of defects manifested by bound electron-hole recombination in the low temperature photoluminescence (PL) spectra. The relative intensities of the PL bands depend strongly on the annealing history of the samples. Confirmation of the involvement of both Cd and Li has been obtained through the measurement of isotope shifts in the spectra for both elements. The energy level structures are complex in some cases and there is evidence that mixed Li isotopes may result in the appearance of transitions which are forbidden for samples produced using only a single Li isotope. This is attributed to the lowering of the defect symmetry in the mixed isotope case due to the presence of different Li isotopes in the defect. Consequently, more than one Li atom is involved in such defects. The results exemplify the complex interactions which Li displays in combination with other impurities in silicon.

14:45-15:15

BREAK

SESSION IX - Proton Implantation

Chairperson: J. Weber, Max-Planck-Institut, Stuttgart, Germany

- A-IX.1** 15:15-15:45 - Invited - **THE EVOLUTION OF DEFECT STRUCTURES IN SILICON AFTER LOW-TEMPERATURE HYDROGEN IMPLANTATION**, **K. Bonde Nielsen** and B. Bech Nielsen, Institute of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark
Low-temperature proton implantation in silicon initiates two deep donor centres E3' and E3'' observed by *in-situ* deep-level transient spectroscopy. Having very similar emission rates these centres are discernible only because the form and anneal differently. During annealing, or free-carrier injection, E3' may be converted into E3'' or vice versa. We show by detailed studies of annealing kinetics that E3'' is a perturbed form of E3', with nearby oxygen being responsible for the perturbation. Further support for this conclusion has been obtained from correlation of the annealing properties of E3'' with the appearance of infrared local vibrational modes ascribed to a structure of weakly interacting bond-centre hydrogen and interstitial oxygen. We suggest, supported by experimental data, that ultra-fast migration of neutral hydrogen through the low electron-density region of the silicon lattice plays an important role in the formation of the defect. We discuss the formation process in detail and argue that elongated Si-Si bonds near interstitial oxygen may promote the formation of defects with electronic properties very similar to those of undisturbed bond-centre hydrogen. It appears that stretching of Si-Si bonds by local perturbations may also in other cases promote the formation of bond-centre like defects. A candidate for such a defect is the hydrogen-carbon E3 centre.
- A-IX.2** 15:45-16:05 **C-H COMPLEX IN SI OBSERVED AT LOW TEMPERATURES**, **L. Hoffmann**, E. Lavrov, and B. Bech Nielsen, Institute of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark
Recently, carbon-hydrogen complexes in silicon have been addressed experimentally and theoretically. The formation of such complexes may have strong implications on the migration of hydrogen and, thus, be of technological importance. Hydrogen and carbon impurities take part in a variety of point defects, among which those most prominent are substitutional carbon, C_s, and bond centered hydrogen, H_{BC}, observed after low temperature proton implantation. In this work, the basic hydrogen-carbon defects are produced by low-temperature proton implantation into carbon-rich Si and henceforth studied by 'in-situ' FTIR. Si samples doped with ¹²C were implanted with protons or deuterons at ~20 K. Subsequently, two new absorption lines were observed at 596 and 1884cm⁻¹ in the as-implanted samples. Measurements on similar samples doped with ¹³C showed that the 596 and 1884cm⁻¹ lines represent local vibrational modes of carbon and hydrogen, respectively. The two modes anneal together at about 220 K indicating that they originate from the same defect. The frequencies of the modes are close to those of C_s (607cm⁻¹) and of H_{BC}⁺ (1998cm⁻¹) in Si. Therefore, we tentatively identify the defect as bond centered hydrogen in the vicinity of a nearby substitutional carbon atom. It may be noted that no evidence for a direct carbon-hydrogen bond was found. Hence the structure proposed on basis of theoretical calculations, where hydrogen is located at the bond center between the substitutional carbon and one of its four Si neighbors, remains unobserved.
- A-IX.3** 16:05-16:40 - Invited - **SELF-INTERSTITIALS AND SELF-INTERSTITIALS RELATED COMPLEXES IN IRRADIATED SILICON**, **B.N. Mukashev**, Kh.A. Abdullin, Yu.V. Gorelkinskii, S.Zh. Tokmoldin, Institute of Physics and Technology, MS-AS RK, 480082, Almtý, 82, Kasakstan
In our talk we will review recent DLTS, IR, and EPR studies of silicon irradiated at 77K by electron, H⁺ and He⁺ ions. Stabilization, migration, trapping and release of self-interstitial were explored by monitoring of interstitial Ci, Ali, metastable complex (Sii-Oi) and intrinsic defects. Due to lower ionization level in H⁺ and He⁺ irradiated samples E(0.39) defect and Si-AA12 state, which was tentatively identified as the self-interstitial, are observed. DLTS band with half-width approximately two times larger than for isolated defect is detected in the same samples. This band has the position of maximum at H(0.20 eV) and exhibits several properties expected for Frenkel's pairs. In addition we will identify a number of IR absorption bands with self-interstitial-hydrogen complexes and discuss their structural models. A detailed study of IR-spectra allows us to detect reversible changes of absorption by conduction electrons due to corresponding transformation of hydrogen-related shallow donors previously observed by EPR and electrical measurements[1]. Absorption bands which are appeared in the bond-bending range due to electron transition between ground and excited states give us strong arguments for double charge electronic structure of these donors. Several models for atomic structure corresponding to the hydrogen-related shallow donors will be discussed. We will also discuss the enhancement of the Al migration through the formation of intermediate Al-H complex (AA-16).
[1] Yu.V. Gorelkinskii and N.N. Nevinniy. Physica B 170 (1991), 155-167.
- A-IX.4** 16:40-17:00 **ULTRADENSE HYDROGEN. THE STATE OF IMPLANTED HYDROGEN AFTER SEGREGATION IN PREFORMED CAVITIES**, **G.E. Cerofolini**, SGS - Thomson Microelectronics, 20041 Agrate MI, Italy and F. Corni, S. Frabboni, C. Nobili, G. Ottaviani, and R. Tonini, Dipartimento di Fisica dell'Università, 41100 Modena MO, Italy
Dissolving hydrogen and noble gases from the gas phase into silicon is an endothermic process. Once dissolved in silicon, these gases tend therefore to segregate into cavities. Cavities can in turn be formed by the organization of pre-existing or process-induced (as it happens when the gas is dissolved by ion implantation) vacancies.
An experimental and theoretical study of the filling and emptying mechanisms of hydrogen in cavities formed by helium implantation is reported. Experiments have been done with the aim of attaining the maximum filling of the cavity.

END OF SYMPOSIUM A

SYMPOSIUM A

SYMPOSIUM A
POSTER SESSION

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

Poster Session

17:05 - 18:00

- A/P1** MUSR OF POROUS SILICON, P. Harris, S. Bayliss, S. Cottrell, Solid State Research Centre, De Montfort University, Leicester, UK

The relevance of the structure of porous silicon (PS) to its optical and electronic properties is still not fully understood. PS is known to be well passivated, generally by hydrogen when fresh and by oxygen when aged. Hydrogen is also present in crystalline and amorphous silicon in varying amounts and may be in the form of intrinsic hydrogen, implanted hydrogen or an impurity [1]. The hydrogen perturbs the system and acts as a source of instability. Hydrogen is however very difficult to detect and locate with conventional spectroscopic techniques. Muon spectroscopy provides information on the available sites for hydrogen in materials. When implanted in matter a free electron may combine with the muon to form muonium. This is analogous with a proton forming a hydrogen atom by the addition of an electron. The muonium will then behave in matter as if it were a light isotope of hydrogen. Favoured hydrogen sites within the matrix may then become occupied by the muonium. Here we report characterisation of the hydrogen sites in porous silicon from positive muon implantation studies.

- A/P2** THE ROLE OF HYDROGEN IN THE FORMATION OF POROUS STRUCTURES IN SILICON, V. Parkhutik, Technical University of Valencia, Spain and E. Andrade, Institute of Physics, National Autonomous University of Mexico, Mexico

The role of hydrogen in the formation of porous silicon structures has become an important problem of inquiry as H atoms are passivating the dangling bonds of the surface silicon atoms. The formation of surface hydride species (SiH_x , $x=1,2,3$) is well documented using the Infrared Absorption Spectroscopy and other methods of chemical analysis. Recently Allongue and coworkers have shown that hydrogen atoms not only passivate the surface of silicon undergoing the reaction of electrochemical localized dissolution, but also incorporate into the volume of semiconductor. The mechanism of incorporation is thought to be a random diffusion of hydrogen from the surface to the bulk.

According to our model of porous silicon formation which we are developing systematically during last years, is that the hydrogen incorporation is not just the artefact of silicon dissolution reaction, but the active agent in the process.

In the present work we show by means of hydrogen recoil spectroscopy that the hydrogen atoms are incorporating into the corroding silicon wafer locally, using easy paths which are generated in the vicinity of the pore tips as a result of combined action of electrolyte solution and dynamic mechanical stress generated during the dissolution reaction. Basing on the results of the work we explain the data on evolution of hydrogen content in aging porous silicon layers, dependence of hydrogen content on the crystallographic orientation of silicon wafer and other practically important issues of the porous silicon formation and properties.

- A/P3** SELF-ORGANIZATION AS A MEANS TO SUPPRESS AND CONTROL DEFECT FORMATION IN SILICON, A. Ya. Gubenko, Moscow Institute of Electronics and Mathematics, ul. Kuusinen 25, Moscow 125252, Russia

Self-organization (SO) can occur upon phase transformations and transitions from nonequilibrium into more equilibrium states with lower free energies. SO occurs in a range of independent variables (RIV) and is effected by large-scale fluctuations whose average amplitude varies in the RIV in an oscillating mode. Each value of an independent variable is related with a corresponding set of large-scale fluctuations that form an oscillating sequence of microstates differing in the nature of interatomic interactions. Along each of the branches of oscillations (i.e., ascending or descending), properties, such as concentrations of self-interstitials and vacancies and other point defects, the ionization energies of thermodonors and kinetics of their reactions in solid silicon, vary in similar ways. Along the opposite branches (descending or ascending), the properties vary in the opposite directions. Therefore, at some values of an independent variable there occurs an enhancement of defect formation in the RIV and at other values, a suppression of defect formation is observed.

- A/P4** PRODUCTION AND PROPERTIES OF MONOCRYSTALLINE SILICON DOPED BY OSMIUM, G. Nurkuziev, Physical-Technical Institute, Mavljanova str. 2B, 700084, Tashkent, Uzbekistan; A.A. Paiziev, Positron Physics Laboratory, Institute of Electronics, Akademgorodok, 700143, Tashkent, Uzbekistan

The modification of physical-chemical properties of silicon is carried out by different methods, including the doping with different elements of the periodic system. At present, practically all elements of the platinum group of the periodic system were used as doping elements. The only exception is the element osmium. One of the reasons of this fact, by our opinion, is the high activity and toxicity of osmium, which causes some technological difficulties during the doping.

We carried out the complex investigation of diffusion and solubility of osmium in silicon in a wide range of temperatures. Features of electrically active osmium centres and their effect on electrical and photoelectrical properties of silicon have been found. The stability of the properties on the influence of outward factors (temperature, irradiation) has been investigated. The osmium diffusion in silicon has been investigated in a separate study of accumulation kinetics of individual electrically active centers in a wide range of temperatures. The energy levels of osmium centers in silicon were determined on the basis of photoelectrical measurements data. It is shown, that osmium generates electrically active centers with energy levels 0.18 eV and 0.53 eV in n type Si and 0.18 eV and 0.53 eV in p type Si. We identify the $E = +0.18$ eV center as the complex $\text{Os} + \text{P}$, but the center $E = +0.18$ eV as $\text{Os} + \text{B}$ complex. The model of $E_c = -0.53$ eV center, being the Os -vacancy system, is proposed.

SYMPOSIUM A

- A/P5** HYDROGENATION OF EPITAXIAL SI-LAYERS GROWN BY CVD, T. Vermeulen, J. Poortmans, M. Caymax, J. Nijs, R. Mertens, Interuniversity Micro-Electronics Centre (IMEC), Kapeldreef 75, 3001 Leuven, Belgium and C. Vinckier, Katholieke Universiteit Leuven, Dept. of Chemistry, Celestijnenlaan 200F, Leuven, Belgium
The possibility of epitaxial Si-growth with well-controlled doping concentration on Si-substrates has lead to many new approaches in semiconductor electronics. Depending on the application, the highly doped substrate is used to induce a back surface electric field, or to act as a gettering side, while the device is made in the epitaxial layer. Defects and impurities present in the substrate are transferred to the layer during epitaxial growth. The crystallographic defects present in epitaxial layers grown by CVD on defected Si-substrates have been studied by means of defect-etching and Nomarski microscopy. Impurities from the substrate entering the epitaxial layer are studied with SIMS. The passivation of defects impurities by remote plasma hydrogenation and by hydrogenation induced by firing a silicon-nitride has been investigated as a function of the electrical and morphological characteristics of the epitaxial layer. Observed side effects of the hydrogenation processes such as surface damage and dopant desactivation are discussed.
- A/P6** INFRARED ABSORPTION STUDY OF A DX-LIKE HYDROGEN-RELATED CENTER IN SILICON, V.P. Markevich, M. Suezawa, Institute for Materials Research, Tohoku University, Sendai 980-77, Japan and L.I. Murin, Institute of Solid State and Semiconductor Physics, Minsk 220072, Belarus
An absorption line at 1025.5cm^{-1} have been found in hydrogenated Czochralski-grown Si crystals after irradiation with fast electrons and annealing in the temperature range $300-400^\circ\text{C}$. Substitution of hydrogen by deuterium resulted in a shift of the band to 1027.9cm^{-1} that clearly indicates H(D) incorporation into the defect which gives rise to the band. It is found that the line is related to a local vibrational mode (LVM) due to a DX-like, having a shallow donor and a deep acceptor levels, center. The LVM band is observed only when the center is in the singly negatively charged state. Transformation of the defect into the neutral state resulted in disappearance of the LVM band and appearance of several absorption lines in the range of $245-325\text{cm}^{-1}$. These lines were interpreted to be associated with ground-to-excited-state electronic transitions in an effective-mass-like shallow donor state of the defect. The structure of the center is discussed.
- A/P7** THE INFLUENCE OF SECONDARY RADIATION DEFECTS ON THE REDISTRIBUTION OF IMPURITY IONS DUE TO HIGH TEMPERATURE PROTON IRRADIATION, V.V. Kozlovski, V.N. Lomasov, State Technical University, St. Petersburg 195251, Russia
Experimental investigation of diffusion enhanced by high temperature proton irradiation (RED), using secondary ion mass- spectrometry (SIMS), showed that the redistribution of impurities in silicon displaced two or more extrema near R_p , the projected range of protons. The maximum to minimum impurity concentration ratio was sometimes more than an order of magnitude. Simple theoretical treatments involving uphill diffusion and two-stream processes could explain only small values of extrema. To explain the observed max to min ratios one has to assume too large, not neutral, thus internal electrical fields arise due to impurities, radiation defects, electrons and holes. Such fields should be considered in detailed physical models of RED.
The purpose of this work is to give a theoretical treatment of a physical model of RED with an internal electric field taken into account to support this explanation by different experiments.
- A/P8** EFFECT OF SHALLOW DONORS INDUCED BY HYDROGEN ON P^+N JUNCTIONS, S. Godey, E. Ntsoenzok, CNRS-CERI, 3A rue de la Férollerie, 45071 Orléans Cedex, France; D. Schmidt, Royal Institute of Technology, Electrum 229, 16440 Kista, Sweden; J.F. Barbot, L.M.P., UMR 6630 CNRS, SP2MI, Bd3 Téléport 2, 86960 Futuroscope Cedex, France
We have evaluated the effect of shallow donors induced by proton irradiation on p^+n junctions. We have combined the C-V technique, which provides the shallow donor profile, and a numerical simulation, based on the solution of Poisson's equation, to determine the electric field as a function of depth in the n-type region. This procedure can be applied to study the breakdown voltage of p^+n junctions as a function of proton irradiation, i.e. its energy and dose.
- A/P9** DONOR CENTER FORMATION IN HYDROGEN IMPLANTED SILICON, V.P. Popov, V.F. Stas, I.V. Antonova, V.I. Obodnikov, Institute of Semiconductor Physics, Novosibirsk, Russia, E.P. Neustroev, Yakutsk State University, Yakutsk, Russia
A new application for hydrogen ion beams in silicon-on-insulator material technology named "smart cut" process stimulated the growing interest in investigation of hydrogen related phenomena. The electrical properties of hydrogen implanted silicon wafers were studied in this paper. P- and n-type Cz-silicon and float zone (FZ) silicon samples with free carrier concentration $1.10^{13}-1.10^{15}\text{cm}^{-3}$ were irradiated by 130 keV H_2^+ ions in dose range of $1.10^{16}-1.5.10^{17}\text{cm}^{-2}$. Samples were heat treated at temperatures $350-550^\circ\text{C}$ and than characterized by Hall, CV, SIMS and DLTS measurements. It was obtained that after post-implantation annealing the conversion of p-type silicon (both Cz- and FZ-Si) in n-type occurs in thick layer behind implanted region. The n-layer thickness and free carrier concentration in it depend on hydrogen dose and annealing time. The depth distribution of donors has maximum, plato and abrupt n-p junction. The temperature interval of donor center existence is $380-500^\circ\text{C}$. In n-type silicon an increase in free carrier concentration is not observed. It means that boron atoms most likely take part in formation of complexes responsible for n-type conductivity in this layer. Self-interstitials and hydrogen atoms are the most probable other components. The complicated character of free carriers depth distribution allows to state that different donor centers (hydrogen enhanced thermodonors, interstitial and hydrogen complexes with participation of boron atoms) form, the n-layer.
- A/P10** TIGHT-BINDING MOLECULAR DYNAMICS CALCULATION OF STABLE POSITIONS AND MIGRATION PATHS OF HYDROGEN, A.P. Mukhtarov, Z.M. Khakimov, F.T. Umarova, Sh.M. Makhkamov, N.A. Tursunov, Institute of Nuclear Physics, Ulughbek, 702 132 Tashkent, Uzbekistan
The modern presentation of interstitial hydrogen in crystalline silicon mainly comes from the calculation results by Local Density Functional approximation. Perhaps, these results have need of confirming or testing by other methods because of well-known deficiency of Local Density Functional method related with underestimation of band gap of semiconductors.
This report presents results of the calculation of stable positions and migration paths of hydrogen by tight-binding molecular dynamics in the frame of cluster model. Our results show that hydrogen atom forms bend-bridge-bond with nearest neighbor Si atoms and rotates around Si-Si bond practically without activation. Therefore H seems to occupy bond center in average. Neutral, positive and negative charge states of hydrogen atom form U-negative system and induce deep level into a band gap. Calculated energy of hydrogen migration is very close to experimental one.
Hydrogen molecule formation becomes preferable in neutral charge state. Then it occupies tetrahedral interstitial site and oriented along $\langle 100 \rangle$.

E-MRS'98 SPRING MEETING



SYMPOSIUM B

Light Emission from Silicon: Progress Towards Si-based Optoelectronics

Symposium Organizers

- F. PRIOLO** INFN and Dept of Physics, University of Catania, Catania, Italy
- J. LINNROÖS** Dept of Electronics, Royal Inst. of Technology, Kista-Stockholm, Sweden
- L. CANHAM** Defence Research Agency, Malvern, UK

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SYMPOSIUM B

Tuesday, June 16, 1998
Mardi 16 juin 1998

Morning
Matin

8:45-9:30

WELCOME ADDRESS, F. Priolo, J. Linnros, L. Canham

SESSION I - Light Emitting Silicon: Different Approaches Towards One Goal

Chairperson: F. Priolo, INFN, University of Catania, Catania, Italy

- B-I.1** 9:00-9:30 - Invited - **RADIATIVE PROCESSES IN BULK CRYSTALLINE SILICON, G. Davies**, Physics Department, King's College London, Strand, London WC2R 2LS, UK
This paper presents an overview of the radiative processes at impurities in bulk crystalline silicon, viewed from the perspective of obtaining efficient luminescence at room temperature. The optical properties of impurities can be classified into those involving one or more loosely bound charge carrier, and those with "deep" ground and excited states. The electronic states of centres with shallow particles can be constructed from perturbed band states. As expected, given the shallow particle(s), the luminescence rapidly decreases in intensity as the temperature is increased. The activation energies for the quenching process vary considerably and surprisingly between centres. Thermal quenching at centres with shallow particle(s) may be disguised to some extent by the electronic structure of the excited states of the centres; spin-coupling of the particles may make the transitions from the lowest energy state partially forbidden, with more strongly allowed transitions occurring from higher-lying spin-singlet states. Then, an increase in the luminescence intensity may occur at first with increasing temperature. In addition to thermal quenching, those centres with readily ionisable charges also suffer from Auger emission processes, so that the luminescence efficiency may be small even in the limit of low temperature. Centres with "deep" ground and excited states, including Er, also apparently invariably also undergo thermally-enhanced quenching with increasing temperature. Additionally some centres also suffer non-radiative charge emission at low temperature; it is likely that many of the non-luminescent centres simply undergo de-excitation by charge emission.
- B-I.2** 9:30-10:00 - Invited - **DIFFERENT Er CENTERS IN Si AND THEIR USE FOR ELECTROLUMINESCENT DEVICES, W. Jantsch**, S. Lanzerstorfer, L. Palmetshofer, M. Stepikhova and H. Preier, Inst. f. Halbleiterphysik, Johannes Kepler Universität, 4040 Linz, Austria
At low temperatures, Er in Si produces a big variety of spectra in the 1.5 μm region which can be identified by high resolution spectroscopy as being due to interstitial Er and different complexes of Er with oxygen, intrinsic defects and other light impurities. Although the luminescence yield can be improved by codoping all of these centers show strong thermal quenching of the luminescence above 150..200 K. There is however one type of rather broad spectrum in heavily Er and O doped Si, which is seen up to temperatures of 400 K and above. This spectrum can be excited in Si by hot electrons generated in a reverse biased diode. The same spectrum appears also in other Si related materials like porous Si, amorphous Si, and in silica. In these materials, excitation spectroscopy is possible and it shows also close agreement for this type of spectra. From these findings we infer that Er is incorporated in another surrounding and we propose $\text{SiO}_2\text{:Er}$ nanoprecipitates since the spectra of other candidates, like Er_2O_3 , are clearly different. We discuss consequences for technology.
- B-I.3** 10:00-10:30 - Invited - **THE INTEGRATION OF NANOSCALE SILICON LIGHT EMITTERS WITH ELECTRONIC CIRCUITRY, P.M. Fauchet**, Department of Electrical Engineering, University of Rochester, Rochester NY 14627, USA
The stability, efficiency, speed, and tunability of light-emitting devices made of nanoscale silicon continue to improve. LEDs with respectable characteristics have now been demonstrated, using a variety of fabrication and processing techniques. The first part of this presentation will focus on the advantages and disadvantages of the different types of nanoscale silicon materials and LED architectures. The main justification for the development of Si LEDs is that, in principle, they can be integrated with silicon microelectronics, using silicon fabrication procedures. The second part of the presentation will be concerned with strategies for integrating nanoscale Si LEDs with electronic circuitry. Several recent demonstrations will be reviewed and the prospects for systems integration will be discussed.

10:30-11:00

BREAK

SYMPOSIUM B

SESSION I - Light Emitting Silicon: Different Approaches Towards One Goal (cnt'd)

Chairperson: J. Linnros, Royal Institute of Technology, Kista-Stockholm, Sweden

- B-I.4** 11:00-11:30 - Invited - **MANIPULATION OF SILICON NANOCRYSTAL SIZE, INTERFACE PASSIVATION AND ARRAY MORPHOLOGY, H.A. Atwater**, K.S. Min, E.A. Boer, D. Santamore, M.L. Brongersma* and A. Polman*; Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena CA 91125, USA; *FOM Institute of Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
Silicon nanocrystals have received widespread attention around the world because of interest in their light emission characteristics. At present, we have the capability to tune the particle size and excitonic emission energy for nanocrystal ensembles via several synthesis approaches. I will describe recent progress in synthesis and passivation of size-controlled silicon nanocrystals formed by i) ion implantation, precipitation, and post-precipitation oxidation in insulators and ii) aerosol deposition of vapor synthesized size-classified nanoparticles. Photoluminescence and luminescence decay lifetime measurements suggest that, for all synthesis conditions that enable structural measurements actually confirming the existence of silicon nanocrystals, these materials undergo excitonic recombination with long radiative lifetimes characteristic of vibronic transitions. This is somewhat disappointing for optoelectronic device applications, but I will discuss other promising electronic device applications (e.g., silicon nanocrystal nonvolatile memory) that have benefited from our improved understanding of and effort towards silicon nanocrystal manipulation and characterization.
- B-I.5** 11:30-12:00 - Invited - **VISIBLE LIGHT EMISSION FROM Si/SiO₂ SUPERLATTICES IN OPTICAL MICROCAVITIES, D.J. Lockwood**, Institute for Microstructural Sciences, National Research Council, Ottawa, ON K1A 0R6, Canada
Bright quantum confined luminescence due to band-to-band recombination can be obtained from Si/SiO₂ superlattices.[1,2] To further enhance their light emitting properties, we have studied the effect of placing them in a one-dimensional optical microcavity. The Si/SiO₂ superlattices were grown on various substrates in a magnetron sputtering system. The effect of the additional optical confinement on the photoluminescence (PL) results in a pronounced modulation of the PL intensity with emission wavelength, as a consequence of the standing wave set up between the substrate and air interfaces. The modulation in the case of a quartz substrate is much weaker, because of the low reflectance (~1%) between the superlattice and the quartz. For a Si substrate, absorption of light reduces the PL efficiency, but for an Al-coated glass substrate the PL intensity is twice that of the quartz substrate case. The addition of a high reflector to the latter structure results in narrow band emission. These results show that a suitably designed quantum microcavity can not only considerably increase the efficiency of luminescence in Si/SiO₂ superlattices but can also be used to decrease the bandwidth and selectively tune the peak wavelength.
*Work in performed in collaboration with B.T. Sullivan and H.J. Labbé.
1. D.J. Lockwood, Z.H. Lu, and J.-M. Baribeau, Phys. Rev. Lett. 76, 539 (1996).
2. B.T. Sullivan, D.J. Lockwood, H.J. Labbé, and Z.H. Lu, Appl. Phys. Lett. 69, 3149 (1996)
- B-I.6** 12:00-12:30 - Invited - **LIGHT EMISSION FROM β FeSi₂, K.J. Reeson, J.S. Sharpe, C. McKinty, D. Leong, M.A. Harry and K.P. Homewood**, School of Electronic Engineering, Information Technology and Mathematics, University of Surrey, Guildford, Surrey, GU2 5XH, UK
Light emission from silicon based substrates has long been a "Holy Grail" of the semiconductor industry. In this paper we report the realisation of a working light emitting device operating at 1.5 μ m. This device is based on a conventional silicon p-n junction with small precipitates of direct band gap β FeSi₂, in the recombination region adjacent to one side of the depletion region. This enables a route for direct radiative recombination, with carrier injection being achieved under forward bias.
This paper will discuss the fabrication of light emitting devices based upon the structure described above. It will also examine our latest results on how the structural morphology affects the external quantum efficiency and how the latter varies with temperature.

12:30-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION II - Si - Based Alloys and Multilayers

Chairperson: L. Pavesi, INFN and Dept. of Physics, University of Trento, Povo, Italy

B-II.1 14:00-14:15

IS THERE STILL ANY HOPE FOR BLUE LUMINESCENCE FROM SILICON ?, L. Rebohle, J. v. Borany, A. Markwitz and W. Skorupa, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., POB 510119, 01314 Dresden, Germany

Yes, at least from a closely silicon related material; silicon dioxide!

Recently, a surprisingly strong blue and violet light emission, both photo- and electroluminescence (PL, EL), was observed from thermally grown silicon dioxide, a basic material of all integrated circuits in current silicon technology [1-3]. These layers were modified using ion beam induced enrichment with Silicon and Germanium. In this talk, a thorough view to the topic will be presented focusing on results from PL and EL measurements as well as microstructure evaluation. It will be shown that nanoclusters consisting only of a few atoms, or, in other words, atomic scale defects in vitreous SiO₂, are most likely responsible for this luminescence. Moreover, the role of radiation damage introduced into the SiO₂-layers during the ion beam related formation process is demonstrated to have an important influence on the PL and EL intensity. Simple devices serving as demonstrators of the electroluminescence effect with efficiencies in the order of 10⁻⁴ will be discussed.

[1] W. Skorupa, R.A. Yankov, I.E. Tyschenko, H. Fröb, T. Böhme, and K. Leo, Appl. Phys. Lett. 68 (1996) 2410

[2] L. Rebohle, J. von Borany, R.A. Yankov, W. Skorupa, I.E. Tyschenko, H. Fröb, and K. Leo, Appl. Phys. Lett. 71 (1997) 2809

[3] J. v. Borany, R. Grötzschel, K.-H. Heinig, A. Markwitz, W. Matz, B. Schmidt, and W. Skorupa, Appl. Phys. Lett. 71 (1997) 3215

B-II.2 14:15-14:30

a-SiO THIN FILM LIGHT EMITTING DEVICES FOR SI-BASED OPTOELECTRONICS, M.C. Rossi, S. Salvatori, F. Galluzzi, Dip. Ingegneria Elettronica, Università di Roma Tre, V. Vasca Navale 84, 00146 Roma, Italy and R. Janssen, M. Stutzmann, Walter Schottky Institut, Technical University of Munich, Am Coulombwall, Garching, Germany

Among suitable candidates for light emitting devices, amorphous alloys are particularly attractive since they appear compatible with silicon wafer processing. Here we present recent results on light emitting p-i-n diodes based on a-SiO_x alloys, deposited by low-temperature PECVD technique. Current-voltage characteristics of such diodes are interpreted in terms of electron and hole injection across n-i and p-i barriers by multistep tunneling processes. In these structures electroluminescence (EL) occurs only when a high density of both types of carriers is reached. A simple model able to describe both EL dependence on current and EL spectral distribution is proposed and the design of a complete optoelectronic structure, containing a-SiO_x light emitting diode, a-SiO_x/SiO₂ optical waveguide and silicon-based photoreceiver, is presented. Integration technology and expected performance are also discussed.

B-II.3 14:30-15:00 - Invited -

ELECTRICAL AND OPTICAL CHARACTERIZATION OF LIGHT EMITTING DEVICES BASED ON Si/CaF₂ MULTILAYERS, A.G. Nassiopoulou, V. Tsakiri, V. Ioannou-Souglideridis, P. Photopoulos, S. Menard*, F. Bassani* and F. Arnaud d'Avitaya*, Institute of Microelectronics, NCSR "Demokritos", P.O. Box 60288, 15310 Aghia Paraskevi Attikis, Athens, Greece ; *Centre de Recherche sur les Mécanismes de la Croissance Cristalline, CNRS, Campus de Luminy, case 913, 13288 Marseille Cedex 9, France

Light emitting devices based on periodic nanocrystalline (Si/CaF₂) multilayers on Si (111) were fabricated [1]. The top metal was either ITO or Au and an ohmic contact was formed on the back side of the wafer [2]. Their electrical and optical properties and the influence of processing steps on photoluminescence (PL) will be discussed. Electrical measurements reveal characteristic behavior similar to that of an MIS structure. The CaF₂ thickness within multilayers is a key parameter to the current transport through the devices since it determines the tunneling probability. A structure with 50 periods of (Si/CaF₂) and a CaF₂ thickness above 1.2 nm shows typical MOS capacitor behavior, with the C-V curve composed of three characteristic regions: inversion, depletion and accumulation. The transition from inversion to accumulation is quite sharp, indicative of satisfactory modulation of the interface between Si and multilayers and an unpinned interface. A significant hysteresis effect indicative of charge trapping was also observed. For smaller CaF₂ thicknesses the C-V and conductance curves were distorted. Current-voltage characteristics reveal important phenomena in vertical carrier transport. I-V curves are almost symmetrical, unless a significant current is injected, leading to irreversible changes. Current transport through the device is dominated by different mechanisms depending on the applied voltage. At high bias voltage Schottky emission over the barrier seems to be the dominant mechanism, while at lower voltages tunneling through bilayers and/or Poole-Frenkel emission seems to be more probable. A number of peaks superimposed on the I-V curves are regularly observed in the range of bias voltages between 1 and 4 Volts. These peaks are quite reproducible and are attributed to resonance tunneling through the multilayers.

[1] F. Bassani, L. Vervoort, I. Mihalcescu, J.C. Vial, and F. Arnaud d'Avitaya, J. Appl. Phys. 79, 4066 (1996)

[2] V. Ioannou-Souglideridis, V. Tsakiri, A.G. Nassiopoulou, P. Photopoulos, F. Bassani and F. Arnaud d'Avitaya, Physica St. Sol. (a) 165 (1), 97 (1998)

B-II.4 15:00-15:15

FIRST-PRINCIPLES OPTICAL PROPERTIES OF Si/CaF₂ MULTI-QUANTUM WELLS, E. Degoli and S. Ossicini, Istituto Nazionale per la Fisica della Materia (INFM) and Dipartimento di Fisica, Università di Modena, via Campi 213/A, 41100 Modena, Italy

The optical properties of Si/CaF₂ multiple quantum wells are studied ab-initio by means of the Linear Muffin Tin Orbital method. In particular we investigate the dependence of the optoelectronic properties on the thickness of the Si wells. We find that wells, whose width is of the order of ~20 Å, show new transitions in the optical region having a remarkable polarization dependence. The oscillator strength of these transitions show a dramatic increase as the width of the Si well decreases. A comparison is made with recent experimental work on similar systems. Our results show that quantum confinement and passivation are necessary in order to have photoluminescence in confined silicon based materials.

B-II.5 15:15-15:30

AMORPHOUS Si/INSULATOR MULTILAYERS GROWN BY MOLECULAR BEAM EPITAXY AND ELECTRON CYCLOTRON RESONANCE PLASMA TREATMENT, J.M. Baribeau, D.J. Lockwood, Z.H. Lu, H.J. Labbé, S.J. Rolfe and G.I. Sproule, Institute for Microstructural Sciences, National Research Council Canada, Ottawa, K1A 0R6, Canada

Thin multilayers of a-Si/SiO₂ grown by vacuum deposition and ex-situ oxidation can exhibit visible light emission.* This work describes progress in the all in-situ growth of a-Si/insulator multilayers using ECR plasma oxidation or nitridation and electron gun Si evaporation. Structural characterization using different techniques shows that O and N plasma exposure leads to the formation of a thin SiO₂ and SiN_x layer whose thickness is controlled by process parameters, but is self-limited to ~1 nm and ~2 nm, respectively. Multilayers produced by evaporation of Si and periodic plasma expositions were studied by photoluminescence (PL) spectroscopy. For thin-layer (~2 nm) Si/SiO₂ multilayers no visible PL was observed in most samples in contrast with ex-situ oxidation,* although weak "blue" PL was seen from all samples due to oxide defect recombination. For the nitride multilayers, weak PL was observed in the 800 - 950 nm wavelength range. Depth profiling of a-Si caps on thin insulating layers revealed no detectable contamination in the nitride film layers, but a 1-2% O contamination was seen in the cap of buried oxide films. The incorporation of oxygen is explained by the desorption of volatile SiO_x species through chemical reaction of the residual oxygen with the molten Si in the evaporator. Impurities in the a-Si and the small thickness of the SiO₂ spacer layers in the a-Si/SiO₂ superlattices may both contribute to the poor optical emission properties of these films.

*Z.H. Lu, D.J. Lockwood and J.-M. Baribeau, Nature 378, 258 (1995).

B-II.6 15:30-15:45

RADIATIVE EMISSION PROPERTIES OF a-SiN:H BASED ALLOYS, NANOMETRIC MULTILAYERS AND LIGHT EMITTING DEVICES, F. Giorgis, C.F. Pirri, INFM and Dept. of Physics, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy and C. Vinegoni, L. Pavesi, INFM and Dept. of Physics, University of Trento, Via Sommarive 14, 38050 Povo, Italy

Nanometric multilayer structures of a-Si_{1-x}N_x:H alloys deposited by PECVD have been studied by photoluminescence measurements. Such structures show very high photoluminescence efficiency even at room temperature, attributed to the localization of electron-hole pairs induced by the multilayer structure. Fast monomolecular recombination processes (sub-nanosecond lifetimes) are evidenced with a large spreading of lifetimes. Analysis of photoluminescence and absorption spectra performed both in multilayer structures and in a-Si_{1-x}N_x:H single layers show a low density of defects and no intermixing at the multilayer heterointerfaces. These investigations are backed by a study of the emission properties of N-rich a-Si_{1-x}N_x:H alloys as a function of N content. Finally, a-Si_{1-x}N_x:H multilayer based light emitting devices with high brightness in the visible range were realized and characterized.

B-II.7 15:45-16:00

SCATTERING-CONTROLLED RECOMBINATION OF Δ₂-LH INDIRECT EXCITONS AND ENHANCED QUANTUM CONFINED STARK EFFECT IN TENSELY STRAINED Si_{1-y}C_y/Si(001) QUANTUM WELLS, S. Fukatsu, M. Sugawara and D. Hippo, Dept. of Pure and Applied Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan; K. Brunner and K. Eberl, Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

Tensile-strained Si has attracted vast attention since record electron mobility was reported while one finds difficulties in growing a relaxed SiGe buffer. In this respect, Si_{1-y}C_y alloys are outstanding since they grow on Si and the band-gap bowing allows a tensile-strained channel. In view of Si-based optics, however, SiC/Si offers a new class of quantum wells (QWs) with Δ₂-LH excitons as opposed to Δ₄-HH excitons in compressively strained SiGe/Si QWs.

In this paper, we report anomalous indirect exciton recombination in SiC-based QWs. The Si_{1-y}C_y/Si(001) samples were grown by molecular beam epitaxy using elemental Si and C at 550°C.

For SiC/Si QWs, the Δ₂ valleys along z are pulled down while the light hole is pushed up in energy due to tensile strain. Importantly, the in-plane k-dispersion is centered at the zone center. This indicates a k-conserving vertical optical transition. To the contrary, experimental spectra exhibit a clear signature of no-phonon as well as phonon replica, indicating the relevance of "indirect" valleys which exist along the QW plane. This is clear evidence that the intervalley scattering between [001]-Δ₂ valleys and in-plane Δ₄ valleys controls the radiative recombination of Δ₂-LH excitons which retain the translational symmetry. As expected, weak transition strengths resulted in long-lived decays.

In addition, an "enhanced" quantum-confined Stark effect was observed. A 10meV redshift was obtained. Thus Δ₂-LH excitons are found to be robust against electric field as opposed to Δ₄-HH excitons in SiGe QWs where electric field weakening masks the Stark effect. This indicates that the binding of Δ₂-LH excitons is considerably large despite shallow confinement, in agreement with variation calculations. The results also indicate the relevance of Δ₄ valleys with the light electron mass which more penetrate into Si than Δ₂ valleys.

SYMPOSIUM B

B-II.8 16:00-16:15

ULTRAFAST CARRIER DYNAMICS IN WIDE-GAP HYDROGENATED AMORPHOUS SILICON, J. Kudrna, P. Maly, S. Surendran, Faculty of Mathematics and Physics, Charles University Prague, Czech Republic, I. Pelant, J. Stuchlik, Institute of Physics, Academy of Sciences of the Czech Republic, Prague; A. Poruba, Faculty of Chemistry, Technical University, Brno, Czech Republic

Silicon based light emitting materials have been attracting attention during past few years. Visible photoluminescence (PL) has been reported also in wide-gap hydrogenated amorphous silicon (a-Si:H) with the hydrogen content up to 40%. In this paper, we report on picosecond and femtosecond pump and probe measurements of the dynamics of photoexcited carriers in wide-gap a-Si:H prepared by microwave electron-cyclotron resonance plasma-enhanced chemical-vapour-deposition. We have observed two components in the dynamics of transient absorption under strong picosecond excitation (carrier densities 10^{20} cm^{-3}). The faster component with the intensity dependent effective decay time ($\sim 10^{-10} \text{ s}$), which is interpreted as a bimolecular recombination process with the rate constant $B \approx 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, is followed by a slower ($\geq 10^{-9} \text{ s}$) component. We associate the former recombination process with the carriers above the mobility edge and the latter process with the trapped carriers. For carrier densities $\leq 10^{18} \text{ cm}^{-3}$, both femtosecond and picosecond measurements suggest the absence of the faster component. We have not found any change in the dynamics when tuning the excitation wavelength through PL excitation spectrum profile. We compare the results with those obtained under the same experimental conditions in other forms of noncrystalline silicon (standard a-Si:H, porous silicon etc.).

16:15-16:30

BREAK

POSTER SESSION I

16:30-19:00

See programme of this poster session p. B-20 to p. B-27 (B-I/P1 to B-I/P42).

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION III - Erbium Doping of Silicon

Chairperson: W. Jantsch, Johannes Kepler Universität, Linz, Austria

- B-III.1** 14:00-14:30 - Invited - **LUMINESCENCE AT 1.54 μm FROM Er DOPED CRYSTALLINE SILICON: PHYSICS AND DEVICES**, G. Franzó, S. Coffa, CNR-IMETEM, Stradale Primosole 50, 95121 Catania, Italy and F. Priolo, INFN and Dipartimento di Fisica, Università di Catania, Corso Italia 57, 95129 Catania, Italy
Erbium doping of crystalline Si has been recently recognized as a very powerful approach towards a VLSI compatible Si-based optoelectronics. In this work the excitation and de-excitation processes of Er^{3+} in crystalline Si will be discussed and correlated to the performances of light emitting diodes. In particular we have found that Auger de-excitation with energy transfer to free carriers is one of the main non-radiative quenching processes of the Er luminescence and is characterized by an Auger coefficient of $\sim 5 \times 10^{-13} \text{ cm}^3/\text{s}$. We have applied this knowledge to the fabrication of room temperature operating Er-doped light emitting Si diodes. These devices emit light at 1.54 μm under both forward and reverse bias conditions. We have studied the line-shape, efficiency and excitation mechanisms in both cases. In particular under reverse bias Er is excited by impact with hot electrons within the depletion region. By maximizing the amount of Er present in the depletion region of the device we have increased the efficiency up to $\sim 0.1\%$ at room temperature. Moreover, by taking full advantage of the Auger quenching, modulation at ~ 10 MHz will be demonstrated. These data will be reported and the future trends of this approach discussed. Moreover the possibility of tuning the wavelength of emission by incorporating different rare earth ions in silicon will be investigated and preliminary results will be reported.
- B-III.2** 14:30-14:45 **EXCITATION MECHANISM OF Er IN Si STUDIED WITH A FREE-ELECTRON LASER**, T. Gregorkiewicz, I. Tsimeridis, D.T. Xuan Thao, and C.A.J. Ammerlaan, Van der Waals - Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands
The results as obtained by double-beam optical spectroscopy on silicon samples implanted with erbium ions are presented. In the experiment the luminescence excited in the visible range by a Nd:YAG or a solid state laser has been studied under the influence of intense infrared (IR) pulses generated by a free-electron laser operating within the 7.5-17 μm range. Depending on the oxygen concentration in the substrate different response has been concluded. For the oxygen-lean material it was observed that the infrared beam quenched the Er-related PL. The effect has been attributed to the dissociation of an Er bound exciton state intermediating the core excitation. Using this effect the kinetics of thus far experimentally inaccessible state has been studied and its lifetime established. In the wavelength dependence of the quenching effect a special feature has been found for $\lambda_{\text{FEL}} \approx 12.5 \mu\text{m}$. This effect was much more pronounced for an equilibrium situation (under continuous laser illumination) than under pulsed (YAG) excitation conditions, and was observed to be strongly temperature-dependent. It was manifested as a less efficient quenching for low temperature /low IR power range, which then changed into a more pronounced quench at higher temperature /high IR power for the particular wavelength of the free-electron laser beam. It is considered whether the observed feature could to represent a direct fingerprint of the so-called "back transfer" mechanism which constitutes an alternative relaxation route for the excited Er core.
- B-III.3** 14:45-15:00 **EPR STUDY OF ERBIUM-IMPURITY COMPLEXES IN SILICON**, J.D. Carey, R.C. Barklie, J.F. Donegan, Department of Physics, Trinity College, Dublin 2, Ireland; F. Priolo, INFN and Dipartimento di Fisica, Università di Catania, Italy; G. Franzó and S. Coffa, CNR-IMETEM, Stradale Primosole 50, 95121 Catania, Italy
Electron paramagnetic resonance (EPR) measurements have been used to characterise Er complexes formed in FZ silicon by implantation of erbium with either oxygen or fluorine. The samples have a 2 μm thick layer containing 10^{19} Er/cm^3 alone or, in addition $3 \times 10^{19} \text{ O/cm}^3$, 10^{20} O/cm^3 or 10^{20} F/cm^3 . Various post-implantation anneals were carried out. No EPR spectrum which could be attributed to isolated Er centres was observed in the sample implanted only with Er and only a broad line anisotropic spectrum was observed in the sample containing $3 \times 10^{19} \text{ O/cm}^3$. For samples annealed at 450 $^\circ\text{C}$ (for 30 mins), 620 $^\circ\text{C}$ (3 hours) and 900 $^\circ\text{C}$ (30 s) sharp line EPR spectra were observed in samples containing 10^{20} O/cm^3 or 10^{20} F/cm^3 . For the O implanted sample the spectra were attributed to two different Er^{3+} complexes. One centre exhibits monoclinic C_{1h} symmetry with principal g-values $g_1=0.80$, $g_2=5.45$ and $g_3=12.60$ and tilt angle $\tau=56.9^\circ$. The second centre exhibits trigonal symmetry with $g_1=0.69$ and $g_2=3.24$. In the F co-implanted sample the spectra was attributed to an Er^{3+} centre with monoclinic C_{1h} symmetry with $g_1=1.35$, $g_2=9.60$ and $g_3=7.75$ and $\tau=79.4^\circ$. The effects of various annealing treatments are presented and possible models for the centres discussed.
- B-III.4** 15:00-15:15 **THE INFLUENCE OF OXYGEN ON THE LATTICE SITES OF RARE EARTHS IN SILICON**, U. Wahl, A. Vantomme, G. Langouche, University of Leuven, Instituut voor Kern- en Stralingsfysica, Celestijnenlaan 200 D, 3001 Leuven, Belgium; J.G. Correia and the ISOLDE Collaboration, CERN, 1211 Genève 23, Switzerland
We have used conversion electron emission channeling to investigate the lattice sites of ^{167}mEr following implantation of the radioactive isotope ^{167}Tm into CZ Si and FZ Si at varying doses ($6 \times 10^{12} - 5 \times 10^{13} \text{ cm}^{-2}$). For annealing temperatures up to 600 $^\circ\text{C}$ no influence of O on the Er lattice sites could be detected, but isothermal annealing at 900 $^\circ\text{C}$ showed up characteristic differences between FZ and CZ Si. In both cases prolonged annealing at 900 $^\circ\text{C}$ caused Er to leave its preferred near-tetrahedral sites in favour of random lattice sites, but this process occurred by orders of magnitude faster in CZ Si. In addition, while in FZ Si the incorporation of Er on random lattice sites was fastest in samples implanted with high doses of Tm/Er, in CZ Si it was fastest for low dose implantations. Qualitatively, this behaviour can be explained by the preferential formation of rare earth silicide precipitates in FZ and rare earth oxide precipitates in CZ Si. For quantitative description we use numerical modelling of O and Tm/Er diffusion and precipitation. Our results support the interpretation that small Er oxide precipitates might be involved in the enhancement of Er luminescence which is observed in O-rich samples annealed at 900 $^\circ\text{C}$.

SYMPOSIUM B

B-III.5 15:15-15:30

DESIGN, PREPARATION, PURIFICATION, CHARACTERIZATION AND UTILIZATION OF DOPANT PRECURSORS FOR CVD OF Si:Er, W.S. Rees, Jr. and O. Just, School of Chemistry & Biochemistry and School of Materials Science & Engineering and Molecular Design Institute, Georgia Institute of Technology, Atlanta GA 30332-0400, USA and L.C. Kimerling and M.T. Morse, Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139, USA

One of the most challenging barriers to silicon based optoelectronics is the achievement of efficient, reproducible emitters. One approach to this problem has been to employ rare earth dopants in a silicon lattice. The benefit of reliance on the highly developed silicon microelectronics industry-driven infrastructure can be realized only if the new device fabrication process is compatible with existing technologies. As such, we have focused on chemical vapor deposition (CVD) as the technique for materials growth. The selection of erbium as a dopant element is driven by a desire to wavelength match the presently utilized silica based optical transmission fibers at 1.54 microns. In order to achieve the desired film properties, a new class of dopant precursors has been designed and developed. This lecture will compare XRD, PL and EL results on CVD films of Si:Er grown from precursors based on erbium- beta-diketonates, -cyclopentadienyls, and -amides. New amide precursors will be presented, and their benefits, relative to other, existing options, will be discussed. The high materials quality of the resultant films and the optoelectronic properties of the devices will be correlated with precursor structure.

B-III.6 15:30-15:45

1.54 μm LIGHT EMISSION FROM Er/O AND Er/F DOPED Si LAYERS GROWN BY MBE, W.-X. Ni, C.-X. Du, K.B. Joelsson, G. Pozina, G.V. Hansson, Dept of Physics, Linköping University, 581 83 Linköping, Sweden

By using a low temperature growth process, the Er doping concentration in MBE Si using Er_2O_3 or ErF_3 as dopant sources has reached a level of $5 \times 10^{19} \text{ cm}^{-3}$ without precipitation and generation of other extended defects. Various light emitting devices were processed using these Er-doped Si structures. Intense electroluminescence (EL) at 1.54 μm has been observed at room temperature under reverse bias. In order to provide more understanding of the luminescence excitation and de-excitation mechanisms, time-resolved EL measurements of these Er-doped MBE Si structures, using an experimental set-up with a time response of 200 ns, have been carried out with different excitation powers at a wide range of temperatures (2-300 K). Device structures involved in this study were designed with an Er-doped layer either in the depletion region for hot electron impact excitation, or in the diffusion region such that the Er ions were excited via energy transfer due to carrier recombination. EL decay processes associated with the spontaneous Er emission ($\sim 700 \mu\text{s}$), the free carrier induced Auger effect ($\sim 4 \mu\text{s}$), the energy back transfer through the Er-related bound exciton (down to 1 μs at 300K), and the hot carrier effects ($\sim 500 \text{ ns}$) have been identified. The role of non-radiative growth-induced point defects will also be discussed. Based on the experimental results, a multi-state energy transfer model has been developed to describe the overall decay behavior of Er-related luminescence.

B-III.7 15:45-16:00

EXCITATION CROSS-SECTION AND LIFETIME OF THE EXCITED STATE OF ERBIUM IONS IN AVALANCHING LIGHT-EMITTING Si:Er:O DIODES, N.A. Sobolev, Ioffe Physicotechnical Institute, 194021 St. Petersburg, Russia, A.M. Emel'yanov and K.F. Shtel'makh, St. Petersburg State Technical University, 195251 St. Petersburg, Russia, P.E. Khakuashev and M.A. Trishenkov, Scientific and Manufacturing Enterprise "Orion", 111123 Moscow, Russia

The diodes showing electroluminescence (EL) of Er^{3+} ions at room temperature have been fabricated by Er^+ , O^+ , and B^+ co-implantation into n-Si and subsequent annealing at different conditions. Electrical and EL measurements were performed at different temperatures. To estimate the excitation cross-section (σ) and lifetime of the excited state (τ), we measured the EL rise time as a function of the current density after applying a square current pulse. Under avalanche breakdown at 300 K, σ is equal to $2.3 \times 10^{-16} \text{ cm}^2$ and τ is equal to 380 μs . A comparative analysis of these parameters for the tunnel and avalanche diodes is made and some future ways for development of light-emitting diodes are discussed.

16:00-16:30

BREAK

SESSION IV- Nanocrystals: Band Structure

Chairperson: Nobuyoshi Koshida, Tokyo University of A & T, Koganei, Tokyo, Japan

- B-IV.1** 16:30-17:00 - Invited - STRUCTURAL DEPENDENCE OF OPTICAL BANDGAPS OF Si NANOCCLUS-
TERS, C. Delerue, M. Lannoo and G. Allan, IEMN - Dept. ISEN, 41 boulevard Vauban,
59046 Lille Cedex, France

We discuss the nature of the optical transitions in porous silicon and in Si nanoclusters in the light of recent theoretical calculations. In a first part we present a detailed review of the calculated dependences of the bandgap with respect to the size of the nanostructures and we discuss their relative accuracy. In a second part we show that the predictions for spherical nanocrystallites are in good agreement with the absorption thresholds measured on oxidized porous silicon or on oxidized silicon crystallites while the photoluminescence energies present an important Stokes shift which increases for smaller sizes. To explain this shift we present tight binding and ab-initio calculations on self-trapped excitons and surface defects. We find that a defect related to an oxygen impurity bound to a silicon atom at the surface could explain the observed luminescence. Our results show that silicon oxide does not necessary lead to a good passivation for small silicon nanostructures. In a third part, we analyze how the electronic structure and the optical properties of silicon clusters depend on their atomic structure. Calculations are presented on clusters in the BC8 crystallographic phase which have improved optical transition probabilities because the bulk material is characterized by a direct bandgap. We also study SiGe and amorphous silicon clusters and obtain strong variations of the bandgaps with size in spite of the disorder. The consequences of these results on the interpretation of the experimental data on these materials are discussed.

- B-IV.2** 17:00-17:15 INFLUENCE OF THE NON-PARABOLICITY ON THE SIZE-ENERGY RELATION-
SHIP IN A QUANTUM BOX: A ONE-BAND DESCRIPTION, N. Maillard, P. Valiron,
Laboratoire d'Astrophysique, UMR 5571-CNRS, Observatoire de Grenoble-Université
Joseph Fourier, BP 53, 38041 Grenoble Cedex 9, France and G. Fishman, Laboratoire
de Spectrométrie Physique-UMR C5588, Université Joseph Fourier-Grenoble 1-CNRS,
BP 87, 38402 Saint-Martin d'Hères Cedex, France

Within the effective mass approximation the confinement energy of a spherical quantum box with infinite potential barriers scales with $1/D^2$ where D is the diameter of the box. Besides, it is known that calculations taking into account twenty bands in the pseudo-potential description or the tight-binding one lead to an energy proportional to $1/D^{1.4}$ with D of the order of a few nanometers in silicon quantum dots.

We present a new model where we take into account i) the finite potential barrier and ii) the non-parabolicity of the (conduction) band within a one-band description: this description is obtained through a sixth-order perturbation in the k.p theory framework. This allows us to perform analytical calculations either in case i) or in case ii) and leads to a very simple insight into the departure from the $1/D^2$ law. In fact, each case leads to a $1/D^{1.7}$ law. Once the cases i and ii are taken into account together, a numerical calculation shows that a $1/D^{1.4}$ law is obtained. This last result shows that the k.p theory can describe a large kinetic energy within a one-band model if we accept to go beyond the effective mass approximation. Therefore the pseudo-potential description and the tight-binding description are not the only ones which provide an adequate framework for the understanding of the size-energy dependence in a small quantum box.

- B-IV.3** 17:15-17:30 SOFT X-RAY EMISSION STUDIES OF THE ELECTRONIC STRUCTURE OF SILI-
CON NANOCRYSTALS*, T. van Buuren, L.N. Dinh, L.L. Chase, L.J. Terminello,
Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Silicon nanocrystals have attracted considerable attention because of their visible photoluminescence (PL). It is generally accepted that quantum confinement of the Si electronic structure is responsible for the light-emitting properties. We find soft x-ray emission (SXE) and absorption (XAS) to be superior to electron spectroscopies and optical techniques in determination of the electronic properties of nanocrystals because it is an element specific bulk probe of the electronic states. In the x-ray emission measurements we are able to selectively probe the silicon independent of any surface oxidation or contamination by suitable choice of the excitation wavelength. A comparison of SXF spectra for the Si nanocrystals with the spectra of bulk Si show that the valence band edge in the nanocrystal shifted to higher binding energy relative to bulk Si. Significant changes in the shape of the spectra are also observed between the Si nanocrystals and bulk Si. We interpret the shift and changes in the spectra of the valence band as resulting from an altered electronic band structure in the confined Si structures. A smaller but proportional shift of the conduction band to higher energy is also observed in the XAS spectra of the silicon nanostructures. Characterization of the size and morphology of the synthesized material was done in situ using STM and ex-situ using atomic force microscopy. We compare the experimentally measured bandgap as a function of particle size to recent electronic structure calculations and find that the experimentally measured bandgap is smaller than that predicted by theory.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-7405-ENG-48.

17:30-18:00

BREAK

SYMPOSIUM B

18:00-19:30

OPEN DISCUSSION on

"Si-based Optoelectronics: how can we get there?"

with an introduction by:

P. Malinverni, European Commission, DG III, EC, Brussels, on:

"European programmes on Si-based optoelectronics"

Kick off by: **Leigh Canham**

All participants are welcome to contribute to a fruitful discussion.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION V - Porous Si: Optoelectronic Properties

Chairperson: R. Romestain, Laboratoire de Spectrométrie Physique, Université J. Fourier - CNRS, St Martin d'Hères, France

- B-V.1** 8:30-9:00 - Invited - **FIELD-INDUCED FUNCTIONS OF POROUS Si AS A CONFINED SYSTEM, N. Koshida**, Tokyo University of A & T, Koganei, Tokyo 184, Japan
It is shown that the quantum-sized properties of luminescent porous Si (PS) have been made clear by experimental observation of some useful electronic functions induced by a high electric field. The experimental PS diodes are composed of thin ITO or semitransparent thin Au films, relatively thin PS layers, n- or p-type Si substrates and ohmic back contacts. The PS layers were formed by conventional anodisation in ethanoic HF solutions. The electrical properties of these diodes were studied in relation to the EL characteristics. When the PS-LEDs formed on the n-Si substrates are driven in vacuum, electrons are uniformly emitted through the top contact as well as photons. At sufficiently high bias voltages, the electron emission becomes dominant over the visible EL. The bias voltage dependence of the emission current follows the Fowler-Nordheim scheme. The emission can be significantly enhanced by RTO treatment. By introducing a structural control into PS based on the anodisation current modification, efficient and fluctuation-free stable emission is obtained. The behavior of the output energy distribution curve suggests that electrons are emitted quasi-ballistically. This is a strong indication that the drift length of electrons in nanocrystalline PS under a high electric field becomes extremely long as a result of multiple tunnelling through interfacial barriers. The PS diode is potentially useful not only as a surface-emitting cold cathode, but also as a ballistic electron device. High-field conduction in PS produces other useful functions associated with carrier injection and ejection phenomena in Si nanocrystallites. The one is a reversible negative-resistance effect and another is a nonvolatile bistable memory effect. These functions closely relate to the EL emission as well. In the case of memory, particularly, the use of either electrical or optical signal is available for writing and reading of information.
- B-V.2** 9:00-9:15 **CHARACTERISATION OF ITO/POROUS SILICON LED STRUCTURES, K. Molnar**, T. Mohacsy, P. Varga, E. Vazsonyi, K. Ferencz* and I. Barsony, Research Institute for Technical Physics and Materials Science - MFA, *Research Institute for Solid State Physics - SZFKI, P.O. Box 49, 1525 Budapest, Hungary
P- and n-type 5 Ωcm <100> Si wafers were etched anodically for 4-15 minutes with a current density of 20 mA/cm². 1:1 HF:C₂H₅OH and 1:1:2 HF:H₂O:C₂H₅OH electrolyte composition was used for p- and n-type wafers, respectively. In order to facilitate the formation of smaller particles, both p and n wafers were illuminated during anodisation by halogen lamps from a distance of 15 cm. The effect of light assistance was obvious, although on p-Si higher intensity was required (250 W) for adequate results. The 3-4 mm diameter LEDs were contacted by 150 nm thick low resistivity ($\rho < 30 \text{ m}\Omega\text{cm}$) transparent ITO, on which small Al contacts were evaporated through shadow masks. In both types of LEDs distinct frequency dependent C-V characteristics were obtained with reverse bias. At 1 MHz the capacitance is apparently lower than at 10 kHz. An equivalent circuit that accounts for this frequency behaviour is suggested by introducing a current dependent conductance $g_p(f)$ for the porous layer. Electroluminescence light intensity modulation bandwidths in the range of 30-40 kHz were measured. The analysis of the DC I-V curves and the several harmonic frequencies in the modulated current revealed the complexity of carrier transport in the devices. Moreover, the role of higher order harmonics is apparently enhanced during extended operation. The role of structural changes in altering the contribution of dominating conduction mechanisms will be discussed.
- B-V.3** 9:15-9:30 **STRONGLY NONLINEAR PHOTOLUMINESCENCE INTENSITY INCREASE IN POROUS SILICON FILMS UNDER HIGH EXCITATION CONDITIONS, H. Koyama**, L. Tsybeskov, and P.M. Fauchet, Department of Electrical Engineering, University of Rochester, Rochester NY 14627, USA
A very strong increase in photoluminescence (PL) intensity is observed in partially oxidized, free-standing porous silicon (PSi) films above an excitation threshold. This indicates that initially nonluminescent Si crystallites can become efficient luminescent centers under high cw excitation. The PSi samples were prepared by anodization of p⁺-Si wafers in HF solutions followed by an electrochemical lift-off. The free-standing films were then oxidized in dry O₂ at 800-900°C for 10 min. When the Ar ion laser excitation intensity reached $\sim 10 \text{ W/cm}^2$, the PL intensity showed a remarkable increase with pump intensity that follows a power law with $n \leq 10$. The strong PL is slightly redshifted, suggesting that large-size Si crystallites which are not luminescent at low excitation intensities, are now participating in the PL. This is supported further by the oxidation-temperature dependence of the PL peak, where a clear blueshift is observed with increasing oxidation temperatures. A simple rate-equation analysis shows that the observed phenomenon can be explained by the saturation of nonradiative recombination channels.
- B-V.4** 9:30-9:45 **TWO-PHOTON-EXCITED PHOTOLUMINESCENCE FROM POROUS Si, I. Diener**, Y.R. Shen, Department of Physics, University of California, Materials Sciences Division, Berkeley CA 94720-7300, USA; D.I. Kovalev, G. Polisski and F. Koch, Technische Universität München, Physik-Department E16, 85747 Garching, Germany
Visible photoluminescence (PL) from Si nanocrystals in porous Si usually results from one photon excitations in the blue or near ultraviolet. Linearly polarized excitation yields PL preferentially linearly polarized along the same direction. We have studied generation of visible PL by two-photon excitation in porous Si using a tunable pulsed IR source. While the main properties of the PL (spectrum, lifetimes and wavelength dependence of the lifetimes) excited by one and two photon excitations are identical, the degree of polarization of PL in the two-photon case is significantly higher (up to a factor of two). This enhancement depends on the sample orientation and has a maximum in the <110> direction for samples prepared from <100> Si substrates. The additional anisotropy results from two-photon absorption by aspherical nanocrystallites in porous Si.

SYMPOSIUM B

B-V.5 9:45-10:00

LOCAL ORDER IN LIGHT EMITTING POROUS SI POROUS SILICON STUDIED BY XEOL AND TEY, G. Dalba, N. Daldosso, P. Fornasini, R. Grisenti, Dipartimento di Fisica dell'Università di Trento, 38050 Povo, Italy; F. Rocca, CeFSA, Centro CNR-ITC di Fisica degli Stati Aggregati, 38050 Povo, Italy and A. Flank and P. Lagarde, LURE bât. 209 D, 91405 Orsay, France

The work presents new results of an EXAFS investigation on porous silicon carried out by XEOL and TEY techniques, at the Si K absorption edge. For the first time XEOL spectra of porous silicon have been recorded in a wide energy range (1880-2500 eV) and EXAFS signals have been singled out from them. TEY and XEOL measurements, made simultaneously on the same sample, yield different results: in particular TEY EXAFS is sensitive up to the third coordination shell of Si while XEOL-EXAFS reveals only the contributions the first two coordination shells. This could be interpreted as an evidence of the sensitivity of XEOL technique at the local structure of the very luminescent sites.

The absence of the third coordination shell in the XEOL-EXAFS FTs suggests that the average dimensions of the luminescent nanostructures monitored by XEOL are smaller than those monitored by TEY. Such lack can be also related to a higher static disorder of the luminescent nanostructures.

The dependence of the light emission properties on the main preparation parameters and their influence on the short-range structure of red and yellow porous silicon samples are also investigated.

10:00-10:30

BREAK

SESSION VI - Nanocrystals: Light Emission

Chairperson: W. Skorupa, Institute of Ion Beam Physics and Materials Research, Research Center Rossendorf, Inc., Dresden, Germany

B-VI.1 10:30-10:45

PHOTOLUMINESCENCE AND OPTICAL GAIN IN Si⁺-IMPLANTED SiO₂, P. Knappek, K. Luterova, I. Pelant, Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 16253 Praha, Czech Republic; J. Valenta, J. Dian, Charles University, Faculty of Mathematics and Physics, Dept. of Chemical Physics and Optics, Ke Karlovu 3, 12116 Praha, Czech Republic; D. Müller, J.J. Grob, Laboratoire PHASE (UPR 292-CNRS), 23 rue du Loess, 67037 Strasbourg, France; J.-L. Rehspringer, IPCMS, Groupe des Matériaux Inorganiques, 23 rue du Loess, 67037 Strasbourg, France; B. Hönerlage, IPCMS, Groupe d'Optique Nonlinéaire et d'Optoélectronique, 23 rue du Loess, 67037 Strasbourg, France

Strong yellow and red/IR photoluminescence (PL) is observed in Si⁺-implanted and annealed silica. Three different types of SiO₂ matrix are used for Si implantation: SiO₂ thin films thermally grown on a Si wafer, SiO₂ films deposited on a silica plate by the sol-gel method and a bare amorphous silica plate. Implantation energies of 100 keV at a fluence $\sim 10^{17}$ cm⁻² were used. Temperature dependent PL and PL excitation spectra are compared to typical porous Si samples. The thermal changes of PL in the range 10-300 K (intensity maximum at 160 K and decreases towards higher as well as lower temperatures) can be well explained by the exciton singlet-triplet splitting model similar to porous Si. Positive optical gain of about 50 cm⁻¹ is observed for T=10-300 K under nanosecond pulsed excitation using the variable stripe-length method.

B-VI.2 10:45-11:00

DOSE DEPENDENCE OF ROOM TEMPERATURE PHOTOLUMINESCENCE FROM Si IMPLANTED SiO₂, S.M. Cheylan, N.B. Manson and R.G. Elliman, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia

Fused silica substrates were implanted with 400 keV Si ions to fluences in the range from 5×10^{13} to 6×10^{17} Si.cm⁻². Samples were subsequently annealed to 1000°C for 60 minutes in an Ar ambient and then subjected to a second anneal at 500°C for 60 minutes in forming gas (5% H₂/95% N₂). Room temperature photoluminescence was measured for as-implanted and annealed samples as a function of ion fluence. Photoluminescence (PL) of as-implanted samples showed a broad peak at 720 nm, consistent with previous reports. However, the luminescence intensity exhibited a maximum for an ion fluence of 6×10^{16} Si.cm⁻², increasing with increasing fluence below this fluence and decreasing for higher fluences. Samples annealed to 1000°C showed a similar dependence on ion fluence together with an expected increase in emission intensity and red-shift. These results and the effect of H passivation are discussed.

B-VI.3 11:00-11:15

SIZE DEPENDENT PHOTOLUMINESCENCE OF Si NANOCCLUSERS PRODUCED BY LASER ABLATION, L. Patrone, D. Nelson, V. Safarov, M. Sentis and W. Marine, Groupement Interdisciplinaire Ablation Laser et Applications, UMR CNRS 6631 et UMR CNRS 6594, Faculté des Sciences de Luminy, Case 901, Marseille, France

We developed the new experimental set-up of silicon nanocluster (nano-Si) synthesis based on the conventional laser ablation technique. The deposition of nano-Si was performed by ArF* laser ($\lambda = 193$ nm, pulse duration $t = 15$ ns, FWHM) ablation of the bulk silicon in different background gases: He, Ar, O₂, H₂ or their mixtures. The cluster condensation has been observed at early stage of laser induced plasma expansion by time resolved luminescence measurements from free nano-Si. The back flowing cluster flux promotes a spatial separation of clusters with different size and deposition of films with selected nano-Si size dispersion. From photoluminescence measurements on the nano-Si films deposited in inert atmosphere, we demonstrate that by altering one deposition parameter (laser fluence or background pressure), we are able to tune photoluminescence maxima from IR to UV. Atomic Force and Transmission Electron Microscopies show the corresponding size variation from 4 to 1 nm. These observations clearly prove the dependence of photoluminescence properties on nano-Si size. Finally, we show the influence of the oxidation effects on the reduction of the crystalline Si core and on the modification of the photoluminescence spectra.

B-VI.4 11:15-11:30

FROM MOLECULAR PRECURSORS TO NANOCRYSTALS : PHOTOLUMINESCENCE FROM SILSESQUIOXANES $(\text{SiO}_{1.5})_n\text{R}_{n-m}\text{L}_m$, Ch. Ossadnik, S. Veprek, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, 85747 Garching, Germany and H. Marsmann, E. Rikowski, Institute for Inorganic Chemistry, University Paderborn, 33095 Paderborn, Germany

Silsesquioxanes are molecular units of the composition $(\text{SiO}_{1.5})_n\text{R}_n$ or $(\text{SiO}_{1.5})_n\text{R}_{n-m}\text{L}_m$ where $(\text{SiO}_{1.5})_n$ is a three dimensional, closed molecular skeleton whose terminal atoms are saturated by organoligands R and L, such as alkyl and silyl groups or hydrogen. In the present study we concentrated on silsesquioxanes with $n = 8, 10$ and 12 whose size varied between 0.56 nm ($n=8$) and 0.68 nm ($n = 12$). The size of the corresponding whole molecular unit $(\text{SiO}_{1.5})_n\text{R}_{n-m}\text{L}_m$ ranged between about 0.8 and 4 nm , thus covering the range of the smallest and medium sized nanocrystals. These compounds were synthesized in a well controlled manner and purity, and their PL was studied both in crystalline (porous) solid state as well as in solution. This allowed us to differentiate between the intrinsic PL from the silsesquioxanes and extrinsic effects e.g. due to the interaction with air which results in the formation of silanol groups. All these compounds show an efficient PL in the blue-violet range whose intensity depends on the size of the skeleton and on the nature of the ligands. The PL decay time is in the range of $\leq 1-3 \text{ ns}$. The experimental results will be presented together with a theoretical interpretation and implications for the photoluminescence observed in porous and nc-Si.

B-VI.5 11:30-11:45

OPTICAL PROPERTIES OF Si FILMS PRODUCED BY SIZE-SELECTED CLUSTER BEAM DEPOSITION, V. Paillard and M.A. Laguna, Lab. de Physique des Solides, Univ. P. Sabatier, 31062 Toulouse Cedex 4, France, M. Ehbrecht, B. Kohn and F. Huisken, Max-Planck-Institut, Bunsenstr. 10, 37073 Göttingen, Germany

Molecular beams of size-selected Si clusters are characterized by time-of-flight mass spectrometry (TOF-MS) before and after deposition. The cluster deposited films are investigated using resonant Raman scattering (RRS) and photoluminescence (PL) spectroscopy. Mean sizes measured by RRS and TOF-MS are in a very good agreement. PL spectra exhibit strong differences, since no PL is detected in films of deposited mean sizes of 400 and above 6500 atoms/cluster. For intermediate sizes, the PL maximum is redshifted with increasing mean size, with apparently an optimum efficiency for a specific size distribution. The absence of PL in the smallest clusters has to be confirmed. But, it appears that a limit size exists, above which no radiative recombination occurs, supporting the quantum confinement theory.

B-VI.6 11:45-12:00

ROOM-TEMPERATURE SiGe LIGHT EMITTING DIODES, L. Vescan, ISI, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany and T. Stoica, National Institute of Material Physics, POB Mg.7, Magurele, Bucharest, Romania

To have an efficient SiGe light emitter for the optical communication wavelengths $1.3-1.6 \mu\text{m}$ much effort has still to be invested to optimize the structure. The data published so far have shown that the radiative recombination in SiGe structures is too low, while the nonradiative recombinations of the type Shockley-Read-Hall and Auger are too high. In the present paper the electroluminescence of PIN diodes with either strained SiGe/Si or Ge islands in the i-region have been investigated experimentally and by quantitative modeling. The modeling helped to improve the buffer layer in both cases and this was due to a reduction of the SRH recombination. In the case of diodes with strained $\text{Si}_{0.80}\text{Ge}_{0.20}$ the simulation has shown that the emission at 300K can be increased if the thickness of the SiGe layer is increased. To overcome the thickness limitation due to the plastic relaxation we used the selective epitaxy to deposit strained layers. Indeed, for samples four times thicker than the critical thickness emission was observed to persist up to 300K in contrast to thinner samples. Light emitting diodes with SiGe islands in the active region were previously shown to emit at low injection currents 100 times more than diodes with strained SiGe layers due to the localization of carriers in the islands. Here we will show that in diodes with Ge islands a reduction of the Auger recombination is possible allowing an increased emission at 300K .

B-VI.7 12:00-12:15

C-INDUCED Ge DOTS: ENHANCED LIGHT OUTPUT FROM Si-BASED NANOSTRUCTURES, O.G. Schmidt, S. Schieker, K. Eberl, Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany and N.Y. Jin-Phillip, F. Phillip, Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

Pre-deposition of a fraction of a monolayer of C on a Si (001) substrate causes formation of extremely small islands after growth of only 2 ML Ge. These C-induced Ge dots can be as small as 10 to 15 nm in diameter and 1 to 2 nm in height. Compared to other Si/SiGeC based heterostructures like Ge islands or SiGe/SiC double quantum wells, C-induced Ge dots exhibit a strongly enhanced no-phonon photoluminescence line. We present a stack of fifty layers of these CGe dots, separated by 9.6 nm Si. Each dot layer consists of 0.2 ML of pre-deposited carbon and 2.4 ML of post-grown Ge. Dislocations are not visible in transmission electron microscopy images. Unlike to an identical structure without the pre-growth of carbon, a variety of advantageous aspects such as strain compensation, strongly enhanced no-phonon photoluminescence at around 1300 nm and the possibility of effective waveguiding make this stack of C-induced Ge islands an attractive structure for optoelectronic devices.

SYMPOSIUM B

B-VI.8 12:15-12:30

BLACKBODY EMISSION IN NANOSTRUCTURED MATERIALS, P. Roura, J. Costa, GRM, Dept. D'Enginyeria Industrial, Universitat de Girona, 17071 Girona, Spain; M. Lopez-de Miguel, B. Garrido and J.R. Morante, Dept. d'Electronica, Facultat de Fisica and E. Bertran, Dept. Fisica Aplicada i Optica, Facultat de Fisica, Universitat de Barcelona, 08028 Barcelona, Spain

It is demonstrated that, when photoluminescence experiments are carried out under conditions of reduced thermal conductivity and/or high excitation intensities, the observed radiation is, in fact, blackbody thermal emission. These conditions are sometimes encountered in experiments on nanostructured materials.

This possibility has been discovered with the analysis of previous results concerning 'photoluminescence' of silicon nanopowder. A model has been developed that considers the particles in the powder as independent, so under vacuum the only dissipation mechanism is thermal radiation. The model agrees very well with the observed phenomenology: spectral shape, transient effects and dependencies on pressure and laser power. The local temperature can be determined.

Although the quantum origin of most radiative emissions in nanostructured materials such as porous silicon is well established, a survey of results found in literature seems to indicate that the above explanation applies, as well, to other cases. Experiments are under way on mechanically milled Si-powder, laser-ablated and self-standing porous-Si.

12:30-14:00

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION VII - Porous Si: Ambient Effects

Chairperson: L. Canham, Defence Research Agency, Malvern, UK

- B-VII.1** 14:00-14:30 - Invited - **STABILIZATION AND FUNCTIONALIZATION OF POROUS SILICON THROUGH LEWIS ACID MEDIATED HYDROSILYLATION, J.M. Buriak, M.J. Allen, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA**
Because of the wide variety of potential applications of porous silicon, a number of approaches have been taken towards its rational modification. Highlights of developments since 1990 will be summarized, followed by description of a new and general approach towards Lewis acid catalyzed hydrosilylation of porous silicon developed in our laboratories. EtAlCl_2 mediated hydrosilylation of alkynes and alkenes smoothly yields vinyl and alkyl groups covalently bound to the surface. Because this method is tolerant of a variety of functionalities, nitrile, hydroxy and methyl ester terminated surfaces were prepared without additional protecting groups. The EtAlCl_2 Lewis acid plays a dual role - it mediates the hydrosilylation event, and acts as a reversible protecting group for Lewis basic sites in the unsaturated substrate which can be removed after the reaction by washing with donating solvents. Porous silicon functionalized with hydrophobic groups demonstrates remarkable stability to boiling in aerated aqueous KOH (pH 10). No oxidation and only minor changes in the surface IR spectra were noted whereas for unfunctionalized porous silicon, the porous layer dissolves. Because of the high stability displayed by these surfaces, this methodology represents an important step towards the use of porous silicon in technologically important applications.
- B-VII.2** 14:30-14:45 **PHOTOLUMINESCENCE QUENCHING OF POROUS SILICON IN ORGANIC SOLVENTS: EVIDENCE FOR DIELECTRIC EFFECTS, S. Fellah, R.B. Wehrspohn, N. Gabouze, F. Ozanam and J.-N. Chazalviel, UDTs, BP 399, Algiers, Algeria and LPMC, CNRS-Ecole Polytechnique, 91128 Palaiseau, France**
The photoluminescence of bright red-luminescent porous silicon has been monitored in-situ in a broad set of organic solvents. In order to avoid chemical effects on the porous silicon surface, care was taken in the choice of the solvents, so that they are perfectly innocuous toward silicon. A special cell was used, allowing transfer of the porous silicon sample from ethanoic HF to the selected solvent without exposure to air, and the stability of the photoluminescence in the solvent as a function of time was checked. The photoluminescence energy was little affected by the presence of a solvent, but the intensity was found to change reversibly by over three orders of magnitude, depending upon the solvent used. Comparison with existing data shows that previous work in the literature may have been affected by chemical effects. Especially, water has a strong quenching effect on the photoluminescence of hydrogenated porous silicon, but this quenching effect rapidly decreases under illumination, due to the photoelectrochemical oxidation of the surface. In the absence of such chemical effects, a clear correlation appears between the magnitude of the quenching effect and the low-frequency dielectric constant ϵ of the solvent, the photoluminescence intensity being roughly proportional to ϵ^{-3} over a broad range of variation of ϵ . This behaviour is straightforwardly accounted for in terms of the variation of the Onsager length, which results from the variation of the effective dielectric constant of the medium in the presence of the solvent.
- B-VII.3** 14:45-15:00 **TUNABILITY OF THE PHOTOLUMINESCENCE IN POROUS SILICON DUE TO DIFFERENT DIELECTRIC ENVIRONMENTS, H.A. Lopez, S.P. Duttagupta, and P.M. Fauchet, Materials Science Program and Department of Electrical Engineering; and X.Linda Chen and S.A. Jenekhe, Department of Chemical Engineering, University of Rochester, Rochester NY 14627, USA**
Precise tunability of the emission properties of porous silicon (PSi) is desired and necessary in achieving full integration of silicon based optoelectronic devices. In this report we demonstrate control over PSi emission properties by changing the dielectric environment surrounding the silicon crystallites. This is achieved by making PSi-polymer nanocomposites, where the degree of modification in photoluminescence (PL) depends on the dielectric constant of the polymers. By increasing the dielectric constant of the environment surrounding the crystallites, a blue shift in PL as high as 200 meV has been observed. This blue shift is attributed to the high dielectric constant of the polymers relative to PSi, which causes a partial screening of the excitons and allows the excitonic levels to shift closer to the bandgap. The shift in excitonic levels increases when the dielectric constant of the polymer increases or when the size of the crystallites decreases (higher porosity). PSi-polymer nanocomposites also exhibit an increase in PL intensity which suggests that the inert infiltrated polymers are able to passivate existing nonradiative channels. Advantages, possible applications, and the physics behind the luminescence of the PSi-polymer nanocomposites will be discussed.
- B-VII.4** 15:00-15:15 **LIQUID SENSORS BASED ON POROUS SILICON OPTICAL WAVEGUIDES, H.F. Arrand, T.M. Benson, University of Nottingham, Nottingham, UK; A. Loni, Defence Evaluation and Research Agency, Malvern, UK; M.G. Krueger, M. Thoenissen, H. Lueth, Institut fuer Schicht und Ionentechnik (ISI), Germany; S. Kershaw, British Telecom Laboratories, Ipswich, UK**
Planar, strip-loaded and self-aligned optical waveguides based on porous silicon (PS) material have all recently been reported. Here the introduction of individual liquid solvents (acetone, methanol, isopropan-2-ol and n-heptane) into the pores of PS optical waveguides is shown to dramatically reduce the loss of the waveguides, in a reversible manner. As the solvents evaporate from the pores, so the loss returns to its original value. Both the magnitude and duration of the loss reduction is sensitive to the type of solvent introduced. In some waveguide samples with a very high initial high loss (around 35dB/cm) the measured insertion loss at a wavelength of 633nm falls by 30dB for a 4mm long sample on the introduction of acetone. Theoretical estimates of the interfacial roughness scattering loss in slab waveguides confirm this as the origin of the reductions observed. In contrast the penetration of water into (oxidised) PS is minimal and when water is dropped on the surface of such waveguides no effects are observed. These observations, combined with the fact that a substantial portion of the guided-mode field interacts with the solvent introduced into the pores, indicate an enhanced sensitivity for sensor applications may be achievable.

15:15-15:45

BREAK

SYMPOSIUM B

SESSION VIII - Light Emitting Silicides

Chairperson: A.G. Nassiopoulou, Inst. of Microelectronics, NCSR "Demokritos", Athens, Greece

B-VIII.1 15:45-16:00

GROWTH AND STRUCTURAL CHARACTERIZATION OF SEMICONDUCTING Ru_2Si_3 , D. Lenssen, H.L. Bay, St. Mesters, C. Dieker, D. Guggi, R. Carius, S. Mantl, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, 52425 Jülich, Germany

Recent band structure calculations indicate, that ruthenium silicide (Ru_2Si_3) is semiconducting with a direct band gap. Electrical measurements performed at single crystals confirm the semiconducting behavior and lead to a band gap in the technologically important regime around 0.8 eV ($\approx 1.55 \mu\text{m}$). This makes Ru_2Si_3 a good candidate for siliconbased optical devices, namely LEDs. We present first results on the epitaxial growth of ruthenium silicide films on Si(100) and Si(111) fabricated by the template method, a special molecular beam epitaxy technique. Therefore, we evaporated a few Angstrom ruthenium on a silicon wafer at low temperatures. A thin silicide surface layer was formed by in situ annealing which served as a template for the overgrowing silicide film fabricated by co-evaporation of ruthenium and silicon. We characterized these films by Rutherford Backscattering and Channelling (RBS/C), X-ray diffraction, transmission electron microscopy and optical absorption.

B-VIII.2 16:00-16:15

CORRELATION BETWEEN STRUCTURAL AND OPTICAL PROPERTIES IN ION BEAM SYNTHESIZED βFeSi_2 PRECIPITATES, M.G. Grimaldi, Phys. Dept., Catania, Italy; S. Coffa, IMETEM, Catania, Italy; F. Marabelli, Phys. Dept., Pavia, Italy; L. Miglio, Mat. Sc. Dept., Milano, Italy; V. Meregalli, MPI-FKF, Stuttgart, Germany

The reported PL and EL at $1.5 \mu\text{m}$ of $\beta\text{-FeSi}_2$ precipitates in crystalline silicon high promises for application in silicon based optoelectronics. The important issue is to understand if the intrinsic luminescence is critically determined by the structure and the size of the precipitates. We performed structural (RBS-channeling, high resolution TEM and XRD) as well as optical (PL and absorption) characterization of samples having extremely different size distribution of precipitates. Samples have been prepared by implanting Fe on heated single crystal Si at several fluence (2×10^{15} - $3 \times 10^{16} \text{ cm}^{-2}$). The implanted samples were annealed for different times in the temperature range 800-900°C. We found that the as-implanted damage structure plays a crucial role in determining the nucleation and growth kinetics of precipitates during post annealing. The final structure has a strong influence on the $1.5 \mu\text{m}$ luminescence yield which reaches a maximum for those processes resulting in a high density of small ($<100 \text{ nm}$) $\beta\text{-FeSi}_2$ clusters. The absorption coefficient of precipitates start to increase at $\sim 0.6 \text{ eV}$ although an optical gap of $\sim 0.8 \text{ eV}$ is measured. These results are discussed in term of band distortion provided by the lattice strain, which is in turn induced by a coherent matching to the silicon matrix. In fact our LMTO-ASA calculations display that the gap nature is very sensitive to lattice strain, as the valence band maxima at Γ and Y points do shift in opposite directions for the same strain field.

B.VIII.3 16:15-16:30

FABRICATION OF p-Si/ $\beta\text{-FeSi}_2$ BALLS/n-Si STRUCTURES BY MBE AND THEIR ELECTRICAL AND OPTICAL PROPERTIES, T. Suemasu, M. Tanaka, T. Fujii, K. Takakura and F. Hasegawa, Inst. of Mater. Sci., Univ. of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki 305-8573, Japan

We report on the formation technique of single-crystalline $\beta\text{-FeSi}_2$ balls ($<100 \text{ nm}$) embedded in a Si p-n junction region by MBE.

Semiconducting $\beta\text{-FeSi}_2$ has attracted much attention due to its direct energy gap of about 0.85 eV. For light emitting devices, p-Si/ $\beta\text{-FeSi}_2$ /n-Si double heterostructure is desirable, because high carrier injection into the $\beta\text{-FeSi}_2$ can be expected in this structure.

Fabrication process is as follows. First, 100--thick $\beta\text{-FeSi}_2$ layers were grown epitaxially on n-Si(001) by reactive deposition epitaxy (deposition of Fe on a hot Si substrate) at 470. Then, 30-min-annealing was performed at 850 in UHV. The $\beta\text{-FeSi}_2$ film aggregated into islands with flat surface after the annealing due to the lattice mismatch (2%) between the two materials. The $\beta\text{-FeSi}_2$ islands aggregated further into a spherical shape ($<100 \text{ nm}$), when a 1- μm -thick p-Si overlayer was grown epitaxially at 750 by MBE with HBO_2 irradiation. It was found from TEM observation that the epitaxial relationship between them and single-crystalline nature of $\beta\text{-FeSi}_2$ were preserved even after the annealing and the Si overgrowth. I-V and C-V characteristics revealed that the junction degrades with an increase of the embedded $\beta\text{-FeSi}_2$ balls. Optical properties will be also discussed in conjunction with the diode characteristics.

POSTER SESSION II

16:30-19:00

See programme of this poster session p. B-28 to B-36 (posters B-II/P1 to B-II/P47)

Friday June 19, 1998
Vendredi 19 juin 1998

Morning
Matin

SESSION IX - Porous Si: Microcavities

Chairperson: Ph. Fauchet, Dept of Elect. Eng., Univ. of Rochester, Rochester, NY, USA

- B-IX.1** 8:30-9:00 - Invited - **ALL POROUS SILICON MICROCAVITIES: PHYSICS AND APPLICATIONS, L. Pavesi, INFN and Dept. of Physics, University of Trento, Via Sommarive 14, 38050 Povo, Italy**
 The spontaneous emission of a material can be controlled by placing it in a micron-sized optical cavity. In this talk I will introduce the subject and will present the realization, the physics and the applications of all porous silicon based microcavities. Periodic and random microcavities as well as coupled microcavities will be reported. The emission properties of the cavities have been characterized as a function of the temperature, of the excitation power and of the response time. Modeling of the structure have been performed on the basis of a transfer matrix approximation. Applications of the cavities in light emitting diodes and in non linear optics will be also presented.
- B-IX.2** 9:00-9:15 **LIGHT EMISSION IN PERIODICALLY MICROSTRUCTURED POROUS SILICON, E.K. Squire, P.A. Snow, P.St.J. Russell, Optoelectronics Group, Department of Physics, University of Bath, Bath BA2 7AY, UK, and L.T. Canham, A.J. Simons, C.L. Reeves, DERA, St. Andrews Road, Malvern, WR14 3PS, UK**
 It has been shown experimentally that periodic microstructuring of the porosity in porous silicon (p-Si) resonant cavity light emitting devices (RCLEDs) radically improves their emission linewidth and beam quality[1]. An important issue not yet fully addressed is the precise role played by the microstructuring outside the cavity, given that the luminescence is distributed throughout the whole structure and that the low porosity layers are highly absorbing.
 Using both experimental and theoretical techniques, we have investigated the optical properties of p-Si multilayer structures. We have fabricated a range of periodically modulated p-Si structures and measured their optical properties using reflectivity, photoluminescence (PL) and time-resolved PL measurements over a range of wavelengths, angles and pump powers. Theoretical modelling of the experimental data, carried out using an extended transfer matrix approach incorporating the effects of dispersion, interface scattering, emission and absorption[2], showed good agreement with the data. These results are being used to examine the nature of emission from porous silicon multilayer structures in order to exploit the nature of light propagation within them. This approach will be used to improve current LED designs.
 [1] L. Pavesi, R. Guardini, C. Mazzoleni, Solid State Comms., 97, (1051-1053), 1996
 [2] E.K. Squire, P.St.J. Russell, P.A. Snow, submitted to JOSA B.
- B-IX.3** 9:15-9:30 **IMPROVEMENT OF THE LUMINESCENCE IN P-TYPE AS-PREPARED OR DYE IMPREGNATED POROUS SILICON MICROCAVITIES, S. Setzu, S. Létant, R. Romestain, J.C. Vial, Laboratoire de Spectrométrie Physique, Université J. Fourier-CNRS (UMR 5588), B.P. 87, 38402 St Martin d'Hères cedex, France**
 The properties of porous silicon microcavities are investigated by photoluminescence and optical reflectivity measurements. We also have used the porous silicon microcavities as a matrix and impregnated the pores with Rhodamine 800 laser dye.
 We have realised distributed Bragg reflectors and microcavities with low doped p-type silicon with a remarkable optical quality ($R_{\text{max}}=99.5\%$, $\text{FWHM}=11\text{ nm}$). These results were obtained by controlling the influence of the anodisation temperature on the formation of porous Si for different current intensities. We have monitored the porosity, growth rate, luminescence, refractive index. A strong decrease of the porous Si/bulk Si interface roughness was obtained for low temperature anodisation.
 The filling of the pores of the microcavities with Rhodamine 800 produces a drastic modification of the spontaneous emission spectrum of the optically excited dye by the microcavity effect: the peak emission intensity is increased, the linewidth is narrowed.
 These results demonstrate that the use of all porous silicon or laser dye-porous silicon microcavities for realising photonic devices provides new possibilities for the improvement of their optical properties.
- B-IX.4** 9:30-9:45 **INTERFERENCE FILTERS FROM POROUS SILICON WITH Laterally Varying Wavelength of Reflection, D. Hunkel, R. Butz, R. Arens-Fischer and H. Lüth, Institute of Thin Film and Ion Technology (ISI), Research Centre Jülich, 52425 Jülich, Germany**
 Porous silicon reflection interference filters consist of up to 40 quarterwave layers with alternating high and low refraction index. The refraction index depends on the porosity of the silicon. The reflection wavelength can vary over a wide range and depends on the thickness and refraction index of the porous layers.
 A laterally continuously varying wavelength with linear profile of the filter can be achieved by manipulating the porosity and thickness of the silicon in the lateral direction. Our approach is to vary the Fermi level laterally by applying a potential parallel to the surface of the wafer. The slope of the Fermi level is easily controlled by the magnitude of the potential. The lateral current density and thus the porosity and thickness is linked to the potential between the laterally varying Fermi level and the counter electrode by the well-known current-voltage characteristic of a Silicon hydrofluoric acid contact. The linearity of the etch profile across the wafer is demonstrated and the properties of preliminary reflection filters are shown.

SYMPOSIUM B

B-IX.5 9:45-10:00

PHOTOLUMINESCENCE STUDY OF POROUS Si MULTILAYERS, Z.H. Xiong, S. Yuan, Z.M. Jiang, J. Qin, L.S. Liao, X.M. Ding, X.Y. Hou and Xun Wang, Surface Physics Laboratory, Fudan University, Shanghai 200433, China

A porous Si micro-cavity has been fabricated by electrochemical etching of a p-type molecular beam epitaxial (MBE) grown Si multilayer sample. The MBE grown Si sample has a non-intentionally doped Si layer with a thickness of 490nm which sandwiched by top and bottom multilayers consisting of five 75nm-thick heavily doped (B doping concentration $=1 \times 10^{19} \text{cm}^{-3}$) layers alternating with 96nm-thick lightly doped (B doping concentration $=1 \times 10^{17} \text{cm}^{-3}$) layers. The MBE grown Si sample was then etched in $\text{HF}/\text{C}_2\text{H}_5\text{OH}=1:1$ solution at a constant current of $30 \text{mA}/\text{cm}^2$ for 10 min. An intense photoluminescence peak centered at 810nm with a narrow FWHM of about 20nm has been observed. This narrow peak can be shifted to 760nm with increasing etching current to $50 \text{mA}/\text{cm}^2$. These results reveal that the porous Si micro-cavity can be easily obtained by the electrochemical etching of the MBE-grown Si multilayer at a constant current.

10:00-10:30

BREAK

SESSION X - Er Doping of Si-Based Materials

Chairperson: T. Gregorkiewicz, Van der Waals - Zeeman Institute, University of Amsterdam, Amsterdam, The Netherlands

B-X.1 10:30-10:45

LUMINESCENCE FROM MBE-GROWN Er:O-DOPED SiGe, A. Sticht, E. Neufeld, A. Luigart, K. Brunner, G. Abstreiter, Walter Schottky Institut, TU München, Am Coulombwall, 85748 Garching, Germany

Erbium-oxygen doped Si is known to emit light at a wavelength of $1.54 \mu\text{m}$, coinciding with the absorption minimum of glass fibers. This is of great technological interest. For many device applications, waveguiding is a necessary property. To achieve this, we incorporated germanium as an additional material component. This results in an increased refractive index of SiGe compared to Si.

We have performed photoluminescence studies on SiGe:Er:O structures with a varying Ge content, finding that holes are probably captured in SiGe layers due to the valence band offset between Si and SiGe. By studying the temperature dependence of the luminescence, we gained new information on the activating energies and, thus, on the quenching mechanisms.

In addition, we have performed electroluminescence studies on both Si:Er:O diodes with varying active layer thickness and SiGe:Er:O diodes with varying Germanium content under both forward and reverse bias conditions. The first series of experiments gives information on the region where erbium ions are actually pumped, the second series indicates that incorporation of Ge increases luminescence in forward bias, while in reverse bias different behaviour is observed for strained and relaxed SiGe layers.

Finally, waveguide structures have been processed. Electroluminescence from the polished end facet of the waveguide has been observed at room temperature.

B-X.2 10:45-11:00

Er-DOPED EDGE EMITTING DEVICES WITH A SiGe WAVEGUIDE, C.-X. Du, W.-X. Ni, K.B. Joelsson, F. Duteil, G.V. Hansson, Department of Physics, Linköping University, 581 83 Linköping, Sweden

Er-doped light emitting devices (LEDs) using a SiGe waveguide and edge emission have been fabricated. In order to suppress the major luminescence thermal quenching due to enhanced energy back transfer in the narrow bandgap SiGe materials, the SiGe waveguiding layer was placed next to the Er-doped layer between top and bottom conducting layers in the device structures. Various sizes of mesas with a width of 25 - 100 μm and a length of 600 - 1000 μm were defined by reactive ion etching (RIE) using SF_6 . The devices were then passivated by SiO_2 , and the Al contacts through openings of the oxide layers were patterned by photolithography. The devices were finalized by deep RIE etching at both sides of the long stripes, where the light emission was detected. The typical reverse breakdown voltage of these LEDs was $\sim 6 \text{V}$ and the ideality factor of the forward I-V characteristic was ~ 1.5 . Electroluminescence (EL) at $1.54 \mu\text{m}$ has been observed at room temperature from the edge emission of these devices under the reverse bias condition with a driving current between 2 and 10 mA. Further studies of the efficiency and optical gain of these Er-doped SiGe waveguiding LEDs are under way, and expected to provide useful knowledge for the realization of Si-based opto-electronics.

B-X.3 11:00-11:15

LASER ANNEALED Er-DOPED a-Si:H THIN FILMS, M.J.V. Bell, L.A.O. Nunes, A.R. Zanatta, Instituto de Física de Sao Carlos, Universidade de Sao Paulo, P.O. Box 369, 13560-970 Sao Carlos, S.P. Brazil

Photoluminescence (PL) at 1540nm was achieved from Er-doped hydrogenated amorphous silicon (a-SiEr:H) thin films after annealing using Ar^+ and Nd-YAG lasers. Cumulative thermal anneals in the 100-500°C temperature range were also performed for comparison purposes. The samples were prepared by cosputtering a Si target covered with metallic Er chunks and nitrogen was employed as an impurity enhancer of the Er^{3+} light emission at 1540 nm. The different annealing processes were probed with the help of PL and Raman spectroscopies. Based on the experimental data, it is suggested that the existence of nc-Si greatly enhances the Er^{3+} light emission at $\sim 1540 \text{nm}$. Moreover, the Nd-YAG laser rendered the most efficient procedure to achieve strong Er^{3+} PL. Nevertheless the different (physico-chemical) phenomena that takes place during the thermal and laser anneals the last one have quite interesting advantages. Limited time of operation and limited (and well defined) area of treated regions are within the main advantages that could be very useful in the design and construction of high efficiency SiEr-based devices.

SYMPOSIUM B

B-X.4 11:15-11:30

ROOM-TEMPERATURE ELECTROLUMINESCENCE FROM ERBIUM-DOPED AMORPHOUS HYDROGENATED SILICON, O.B. Gusev, M.S. Bresler, E.I. Terukov, K.D. Tsendin and I.N. Yassievich, AF Ioffe Physico-Technical Institute, Politekhnikeskaya 26, 194021 St Petersburg, Russia

We have studied electroluminescence in the amorphous silicon-based erbium-doped structures at reverse bias in the temperature range 77-300 K. The intensity of electroluminescence at the wavelength of 1.54 μm corresponding to a radiative transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ in the internal 4f-shell of the Er^{3+} ion exhibits a maximum near the room temperature. Theoretical analysis and comparison with the experiment have shown that the excitation of erbium ions occurs by an Auger process which involves the capture of conduction electrons by neutral dangling bonds (D°) defects located close to erbium ions. The stationary current through the structure is kept by a reverse process of thermally activated tunnel emission of electrons from negatively charged dangling-bond defects (D^- defects) to the conduction band of the amorphous matrix. This mechanism is supported experimentally by an unconventional temperature and electric-field dependence of the erbium electroluminescence. A theoretical model proposed explains consistently all of our experimental data.

B-X.5 11:30-11:45

LUMINESCENCE PROPERTIES OF Er^{3+} IN SiN/PS:Er , S. Uekusa, T. Inomata, Meiji University, Department of Electrical Engineering, Kawasaki, Japan

Erbium (Er)-doped porous silicon (PS:Er) has attracted increasing attention as a promising material for light emitting devices in optical communication systems. However PS is typically known to be unstable at high-temperature. The decrease of luminescence from host PS by thermal annealing prevents optical activation of Er ions. We have so far prepared intentionally SiN layers on PS:Er for capping layer by photo-CVD. These PS:Er samples are fabricated by anodically etching and subsequent doping with Er^{3+} by electrochemical method. After deposition of SiN, annealed at 900~1300°C for 60 sec in Ar atmosphere for optical activation. We observed Er-related emissions at 1534nm with a full width at half-maximum (FWHM) of 10nm from the samples with SiN layers and reduction in PL intensity of about a factor of two over the 18 to 300K temperature range. But the samples without SiN layers were no emission. From the results, it is found that the SiN layer on PS:Er is useful for both host PS and Er-related 1.5 μm luminescences.

11:45-12:00

Award presentation

12:00-12:30

Gordon Davies: Symposium Summary

12:30

LUNCH

END OF SYMPOSIUM B

SYMPOSIUM B
SYMPOSIUM B
POSTER SESSIONS

Tuesday June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-midi

Poster Session I
16:30-19:00

Erbium Doping

- B-I/P1** ELECTRICAL AND OPTICAL PROPERTIES OF DEEP TRAPS IN Er- DOPED LPE SILICON, A. Cavallini, B. Fraboni, INFN and Dept. of Physics, University of Bologna, viale Berti Pichat 6/2, Bologna, Italy; S. Pizzini, S. Binetti, INFN and Dept. of Materials Science, University of Milano, via Emanuelli 15, Milano, Italy; L. Lazzarini, G. Salvati, CNR-MASPEC, Via Chiavari 18/A, Parma, Italy
The optical activity of Er-doped silicon is influenced by the presence of defects which determine the intensity of the typical radiative transition at 0.8 eV but whose nature and properties are still largely unknown.
We have studied the deep levels present in Er-doped silicon epilayers grown by the liquid phase epitaxy method by deep level transient spectroscopy and optical DLTS, in order to identify the majority and minority carrier traps and a possible correlation between these traps and the observed photoluminescence (PL) and cathodoluminescence (CL) spectra. Capacitance-voltage analyses have been performed to analyze uniformity and depth distribution of the existing traps and marked differences have been observed between the luminescent and non-luminescent materials.
The PL and depth resolved CL revealed the presence of dislocation-related emission lines which can possibly be correlated to the broadened peaks observed in DLTS analyses of luminescent material.
- B-I/P2** ERBIUM DOPED SILICON EPILAYERS GROWN BY LIQUID PHASE EPITAXY, S. Binetti, A. Cavallini*, A. Dellafiore, B. Fraboni*, E. Grilli, M. Guzzi, S. Pizzini, S. Sanguinetti, Istituto Nazionale di Fisica della Materia, INFN, Dipartimento di Scienza dei Materiali, Via Emanuelli, 15, 20126 Milano, Italy; *Dipartimento di Fisica, Via Berti Pichat 6/2 Bologna, Italy
Liquid phase epitaxy from a Si-In-Er solution has been used to grow 3-7 μm thick epilayers of Er doped silicon onto CZ and FZ silicon substrates. The Er concentration in the liquid solution was preliminarily optimized in order to get a flat Er profile in the epilayer, at a concentration close to $10^{18}\text{at}/\text{cm}^3$. The samples are In-doped, with a In content corresponding to its solubility in silicon ($10^{16}\text{at}/\text{cm}^3$) at the growth temperature (950°C). TEM investigations on cross sections of the epilayers show a very clean substrate-epi interface, virtually free of extended defects, except few stacking faults. Some of the samples grown on CZ substrates presented detectable, but feeble photoluminescence (PL) at 2K in the spectral range of emission of the Er^{3+} manifold at 0.8 eV. Apparently, the poor PL intensity of the material is associated to the absence of oxygen as the nearest neighbour of Er in the as-grown epilayers, as resulted from EXAFS measurements carried out at the ESRF facility in Grenoble (France).
After a proper three-step thermal annealing, designed to back-diffuse oxygen from the CZ-rich substrates and to segregate it as erbium oxide, the local erbium configuration converted to that of erbium oxide and photoluminescence sets up also in samples which were optically inactive in the as-grown state. Also in this case the PL is feeble, in good agreement with DLTS and O-DLTS experiment which show that the density of Er-related recombination centres is around 10^{14}cm^{-3} . These last results let us conclude that not only the structural, but also the electrical quality of the epilayers is very good, but that the density of the active Er centres should be increased at least of two orders of magnitude, by implementing the oxygen doping procedures.
- B-I/P3** 1.54 μm EMISSION OF PULSED LASER DEPOSITED $\text{SiO}_2\text{:Er}$ FILMS ON Si, S. Lanzerstorfer, J. Pedarnig, A. Gunasekaran, D. Bäuerle and W. Jantsch, Johannes Kepler Universität, Linz, Austria
The trivalent Er ion emits at a wavelength of 1.54 μm , independent of the host material. Er doped Si has been investigated in detail because of potential optoelectronic applications. There is, however, a strong temperature quenching of the luminescence yield of Er doped Si. On the other hand, the emission of Er doped SiO_2 is rather temperature stable. This makes Er doped SiO_2 a possible candidate for a room temperature operating optically pumped 1.54 μm source compatible with Si technology.
The pulsed laser deposition (PLD) technique enables the stoichiometric deposition of solid mixtures consisting of components with different vapour pressures, like Er and SiO_2 . The room temperature luminescence of Er doped PLD films depends on the layer thickness, which was adjusted in the range between 100 nm and 700 nm as well as from the oxygen pressure during deposition. The solid solubility of Er increases by switching from a one component glass to a multicomponent type. Therefore the luminescence is strongly enhanced and the line width decreases from 40 nm to 20 nm indicating that certain Er sites are favored in complex glass hosts.
- B-I/P4** DISLOCATION-RELATED LUMINESCENCE IN Er-IMPLANTED SILICON, N.A. Sobolev, O.B. Gusev and E.I. Shek, Ioffe Physicotechnical Institute, St. Petersburg 194021, Russia; V.I. Vdovin and T.G. Yugova, Institute for Chemical Problems of Microelectronics, Moscow 109017, Russia; A.M. Emel'yanov, St. Petersburg State Technical University, St. Petersburg 195251, Russia
Dislocation-related luminescence (DRL) at 1.52 μm (D1 line) and 1.42 μm (D2 line) were earlier observed in plastically deformed silicon and relaxed epitaxial SiGe layers. We have recently found the lines at the same wavelengths in Er-implanted Si. The purpose of this work is to gain insight into the nature of the lines.
We have shown that the Er-implanted Si after annealing at 1100°C has three types of dislocation defects (Frank and perfect prismatic dislocation loops, and pure edge dislocations). Their formation is associated with Si supersaturation with self-interstitials. A correlation between the dependencies of the D1/D2 line intensity and the pure edge dislocation density on the annealing time indicates that the dislocations are responsible for the appearance of DRL.

SYMPOSIUM B

- B-I/P5** EXAFS ANALYSIS OF Er SITES IN Er-O AND Er-F CO-DOPED CRYSTALLINE Si, A. Terrasi and F. Priolo, INFN and University of Catania, Corso Italia 57, 95129 Catania, Italy, G. Franzó and S. Coffa, CNR-IMETEM, Stradale Primosole 50, 95121 Catania, Italy; F. D'Acapito and S. Mobilio, ESRF-GILDA CRG, 38043 Grenoble, France
Er doping of Si has been demonstrated to be a very promising candidate for the realization of a Si-based optoelectronics. The presence of O or F in Er doped Si samples is necessary in order to incorporate high Er contents in crystalline Si and to increase the luminescence efficiency. It is then of primary importance to study the local structure of Er when different co-doping species, at various doses and after several thermal processes, are used. In this work we report an extensive study of the Er chemical surrounding in Si performed by EXAFS analyses. Er and O or Er and F have been implanted in Si at different Er-impurity ratios. The implantation process leaves the samples amorphous and different annealing processes have then been performed. It has been found that the local environment around Er, which consists of 6 Si first neighbors in all of the amorphous samples, evolves towards a mixed coordination with O and Si atoms after the epitaxial regrowth of the layer indicating that a significant Er-O interaction has already occurred during this process. A further thermal treatment at higher temperatures removes the residual Er-Si coordination and produces a full O coordinated first shell. In contrast, in the Er and F doped samples EXAFS data show that Er is fully coordinated with F just after the regrowth process. These data will be presented and related to the photoluminescence results obtained on the same samples.
- B-I/P6** LUMINESCENCE FROM ERBIUM IN SiO_x GROWN BY MOLECULAR EPITAXY, J. Wan, C. Sheng, D.W. Gong, F. Lu, Y.L. Fan, F. Lin, L.S. Liao and Xun Wang, Surface Physics Laboratory, Fudan University, Shanghai 200433, China
Erbium doped SiO_x is prepared by molecular beam epitaxy. Oxygen is introduced into the growth chamber through a leak valve during the growth. The incorporation of Er in the epitaxial films was investigated using Auger spectroscopy and photoluminescence (PL) techniques. It was found that Er react with Q at the Si surface forming complexes which can be easily incorporated. The PL intensity decreases only by a factor of 2 when the temperature increases from 18K to 300K. It means that Er doped SiO_x may be a possible candidate for Si-based optoelectronics. The temperature dependence of the PL intensity shows an exponential decay with an activation energy of 12meV at low temperature (<100K) and 150meV at high temperature (>100K). The relationship between PL intensity and pump power is also discussed.
- B-I/P7** NEW EFFICIENT MECHANISM OF EXCITATION OF ELECTROLUMINESCENCE FROM ERBIUM IONS IN CRYSTALLINE SILICON, M.S. Bresler, O.B. Gusev, P.E. Pak, N.A. Sobolev and I.N. Yassievich, AF Ioffe Physico-Technical Institute, Politekhicheskaya 26, 194021 St Petersburg, Russia
In a specially prepared p-n junctions on the basis of c-Si:Er we have realized a highly efficient new excitation mechanism of erbium ions in a crystalline silicon with an excitation efficiency close to unit. This mechanism is based on Auger recombination of hot electrons occupying the upper sub-band of the conduction band with free holes in the valence band whereas the energy of the recombination process is transferred by Coulomb interaction to an f-electron a nearby erbium ion transmitting it to the second excited state $4f_{11/2}$ (excitation energy 1.24 eV). Experimentally the new mechanism manifests itself in an unusual temperature dependence of the intensity and the switch-on time of erbium luminescence, as also of the resistance of the p-n junction and the hot carrier luminescence. The erbium luminescence from negatively-biased electroluminescent structure is low at low temperatures but exhibits an abrupt jump at and remains fairly high up to the room temperature. This behavior is accompanied by a sharp decrease of the current through the structure at the same temperature indicating the onset of a strong recombination mechanism. The switch-on time of the erbium electroluminescence drops also at the temperature of 160 K. The three-level excitation realized is promising for development of a Si:Er laser.
- B-I/P8** IMPACT EXCITATION OF THE f - f EMISSION IN CLUSTERS Er - O IN SILICON, L.G. Gerchikov and V.F. Masterov, St. Petersburg State Technical University, Politekhicheskaya 29, St. Petersburg 195251, Russia
The Er_2O_3 quantum dot (cluster) with dimensions about 1.2nm in silicon is discussed as a possible source of the Er related emission in Si:Er:O, excited by hot carriers in the light-emitting diodes under reverse bias. This quantum dot is represented as a spherical quantum well 1eV in depth. We proposed a mechanism that gives a simple explanation of the high efficiency of the Er excitation in clusters Er-O. The large value of impact excitation cross section is connected with the presents of resonance electron level localized on the Er-O cluster. The resonance state has the energy 0.8eV above the bottom of the silicon conduction band and angular momentum L=1. The centrifugal potential which separates the quantum dot from the bulk silicon is responsible for the existence of the resonance level. This resonance level plays role of an electron trap. The hot electrons with the energy about 1.6 eV are trapped by the Er-O cluster and transfer their energy to f-shell electrons of erbium. The resonance character of this process causes the large value of excitation cross section $\sigma \approx 4 \text{ \AA}^2$. The suggested mechanism of the enhancement of Er related electroluminescence in silicon due to its universal character may be also valid for another impurities, for example for N, which can form the clusters with Er atoms.
- B-I/P9** EPITAXIAL GROWTH OF LIGHT EMITTING Si:Er LAYERS BY MBE WITH SUBLIMATING SOURCES, L.K. Orlov, A.V. Potapov, S.V. Ivin, Institute for Physics of Microstructures RAS, GSP-105, 603600, Nizhny Novgorod, Russia; V.G. Shengurov, D.V. Schengurov, N.L. Orlova, PTRI NNSU, Nizhny Novgorod, Russia; T.G. Yugova, Giredmet, Moscow, Russia; E. Steinman, ISSP RAS, Chernogolovka, Russia
We have applied MBE with sublimating sources for growth of epitaxial Si films doped by Er. Using this method we have grown light (1.534 μm) emitting Si epitaxial layers at different growth conditions. The growth temperature was varied from 400 to 700°C, the residual gas pressure was changed from 10^{-11} to 10^{-7} Torr. The Er concentration in layers was about $(1-3) \times 10^{19} \text{ cm}^{-3}$. The emissive power of photoluminescence was investigated versus the structure parameters. A comparative analysis of the radiation characteristics of Si:Er layers grown by different methods (ion implantation, liquid phase epitaxy and our method) has been made. In order to study the influence of peculiarities of crystalline and electronic structures on light emitting characteristics of an Er complex we have prepared porous silicon layers from the grown epitaxial Si:Er films. Comparison of the photoluminescence properties of a single crystal and porous silicon doped by Er demonstrated worse radiation characteristics of porous samples. It points to a different nature of the radiation recombination mechanisms in porous silicon preliminary doped by Er and porous silicon doped by Er from the solution during electrochemical etching.
- Porous Silicon**
- B-I/P10** INITIAL STAGES OF POROUS SILICON FORMATION ON PLASMA-MODIFIED Si SURFACES, S. Fellah, N. Gabouze, F. Ozanam, J.-N. Chazalviel, A. Dakhia and Y. Belkacem, UDTS, BP 399, Algiers, Algeria and LPMC, CNRS-Ecole Polytechnique, 91128 Palaiseau, France
An experimental study of the influence of the initial state of the Si surface on pore initiation was performed using combined in-situ and ex-situ characterisation. For this purpose, samples were coated with hydrocarbon groups (CH_x) deposited by a plasma of methane. In HF environment, this coating is stable but can be destroyed upon flowing of an anodic current. In-situ electrochemical characterisations and FTIR absorption spectra were used on p-Si/ (CH_x) during the first stages of anodisation, together with ex-situ SEM observation. After a short anodisation time, the topography of the surface exhibits flat areas with sharp boundaries, with also linear defects and etch pits. After similar electrochemical treatments, unmodified Si surfaces appear comparatively much smoother. Surfaces previously modified with methanol treatment come out rather similar to unmodified surfaces, which suggests that the effect of the hydrocarbon treatment is more a physical inhibition than a chemical effect. These results are compatible with the model that H incorporation is responsible for the generation of structural defects. In practice, they indicate that a methane-plasma treatment can be used as a simple effective means for affecting the initiation of porous silicon formation, and a potential tool for ultra-low thickness masking and patterning.

- B-I/P11** **LASER ASSISTED CVD OF SILICON OXIDE LAYERS**, P. Paiva, F. Madelino and O. Conde, Physics Department, University of Lisbon, Campo Grande, Ed. C1, 1700 Lisboa, Portugal; G. Lamedica, M. Balucani and A. Ferrari, INFM and Electronics Eng. Dept., University of Rome, Via Eudossiana 18, 00184 Roma, Italia
In order to increase the industrial interest by light sources (LS) based on porous silicon (PS), the stability and reproducibility of the PSLs should be improved. A contributing factor to this could be the deposition of a suitable protective transparent dielectric coating on top of the active porous silicon layer.
This paper focuses on the deposition of silicon oxide films on silicon by photothermal laser assisted CVD, using a cw CO₂ laser. Scanning electron (SEM) and atomic force (AFM) microscopies were used for analysing the morphology and microstructure of the films, while structure and chemical composition were determined by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering (RBS). Two wavelength ellipsometry was also used for thickness and refraction index evaluation.
The study of the films demonstrated that their properties are strongly influenced by the total pressure inside the LCVD reactor and by the oxygen to silicon ratio in the gas phase. Optimisation of the processing parameters led to the deposition of adherent silicon oxide films, either dose to stoichiometry ($n=1.46$) or exhibiting a lower refraction index ($n=1.33$).
- B-I/P12** **COMPARATIVE STUDY OF THE OXIDATION OF THIN POROUS SILICON LAYERS STUDIED BY REFLECTOMETRY, SPECTROSCOPIC ELLIPSOMETRY AND SECONDARY ION MASS SPECTROSCOPY**, M. Fried, O. Polgar, T. Lohner, Res. Inst. for Tech. Phys. and Mater. Sci., POB 49, 1525 Budapest, Hungary, S. Strehle, C. Levy-Clement, CNRS-LPSB, 1 Place A. Briand, 92195, Meudon, France
The application of porous silicon (PS) requires a good control of the properties, which depend essentially on the morphology. PS is sensitive to aging effects leading to modification of its properties. Since the properties of non-oxidised PS differ from that of oxidised PS, better knowledge on the influence of oxidation is needed.
We studied ultrathin PS layers (40 - 120 nm) of two different porosities, formed by electrochemical etching and followed by thermal oxidation treatment (300 and 600 °C) and by electrochemical oxidation. The samples have been analysed by spectroscopic reflectometry (SR), spectroscopic ellipsometry (SE) and secondary ion mass spectroscopy (SIMS).
The SR and SE spectra were fitted by a multiparameter fit program and the composition and the thickness of the PS layers were evaluated by different optical models [1]. While the non-oxidised PS can be well described by a simple optical model (one layer of two-components, Si and voids) the spectra of the oxidised PS layers can be fitted better using an optical model with three interdependent components (Si, SiO₂, voids).
The thickness of the oxidised PS layers has been deduced from the SIMS analysis and confirmed by profilometric measurements, too. A comparison of the Si/O signal ratio gives a strong support for the optical model used for SR and SE.
[1] M. Fried et al, Thin Solid Films 276 (1996) 223.
- B-I/P13** **PHOTOLUMINESCENCE FROM PHOTOCHEMICALLY ETCHED POROUS SILICON**, F.M. Oureshi, J.C. Barnard and R.E. Palmer, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK, and K.W. Kolasinski, School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK
We report on the photoluminescence properties of porous silicon produced by photochemical etching of an n type (4-6) Ωcm Si (111) substrate. Etching was performed in concentrated hydrofluoric acid (HF) for various times ranging from 2 minutes to 30 minutes using a Helium Neon laser at 632 nm. Photoluminescence measurements taken immediately after the etching process at room temperature, with argon ion laser excitation at 458nm, show strong red luminescence (~640nm, FWHM ~100 nm) exhibiting an increase in intensity and only slight red shifts with longer etching times. Oxidation in ambient air leads to significant broadening and a red shift of the photoluminescence spectra. This shift is not reversed when the oxide layer is removed by concentrated HF. These results are discussed and compared to porous silicon produced at different wavelengths of 458nm and 514nm at similar etching times and varying input powers.
- B-I/P14** **DIELECTRIC PERMITTIVITY OF POROUS SILICON**, S.P. Zimin, E.P. Komarov, Yaroslavl State University, Sovetskaya str. 14, Yaroslavl, 150000 Russia
The value of dielectric permittivity ϵ of porous silicon (PS) in the range of 30 - 68% weight porosity P is experimentally defined in this work. For this purpose the structures with thick layers of porous material (90 - 180 μm) were used. The frequency dispersion of PS capacity is defined in the frequency F interval of 50 - 700 kHz, which is subject to the law $C \sim F^a$, $a = -(0.3 \pm 0.1)$. Dielectric permittivity decreased from 8.6 to 4.2 when porosity increased. Analysis of experimental dependency $\epsilon(P)$ was conducted on the basis of two-phase material structure. It was shown that when considering pores filled with air ($\epsilon_2 = 1$) one cannot completely adjust experimental and theoretical results. It was found that when the value of effective dielectric medium permittivity inside pores ϵ_2 varies from 2.3 to 4.8 it is possible to describe experimental dependencies in the frames of several models. Obtained results clearly witness of the fact that when analyzing PS capacity, optical and electrical properties one should take into account the existence of dielectric phase at the pores region with the values of dielectric permittivity $\epsilon_2 > 1$.
- B-I/P15** **TIME RESOLVED PHOTOLUMINESCENCE STUDY OF THE RED EMISSION IN NANOPOROUS SiGe ALLOYS**, S. Lebib, H.J. von Bardeleben, J. Cernogora, J.L. Fave and J. Roussel, Groupe de Physique des Solides, Universités Paris 6&7, UMR 75-88 au CNRS, 2 place Jussieu, 75005 Paris Cedex 05, France
The change from the elemental system of porous silicon to the alloy system of porous SiGe is expected to modify the intrinsic photoluminescence (PL) processes via the change in the bandstructure and effective masses as well as by the introduction of disorder, leading to a reduction of the radiative recombination rates. First PL results on porous SiGe for two alloy compositions of 5% and 20% have been reported previously (1). We present here an extension of this study to a wider range of compositions i.e. 5%, 7%, 12%, 20% and 30% Ge and different surface passivations states.
P-type SiGe epitaxial layers with a typical thickness of 1 μm were electrochemically etched to obtain porosities of ~80%. In CW PL the samples presented all a red photoluminescence band centered at $E \sim 1.7\text{eV}$ as well as a weaker blue PL band. For the time resolved measurements the samples were excited with a nitrogen laser (3315Å). The decline of the red PL has been measured for the various compositions as a function of emission energy and temperature (15K...300K) in the μs -ms time range. The PL decay is non exponential and has been fitted by a stretched exponential function. We have further studied the influence of the surface passivation on the recombination rate by comparing the PL decline in as prepared and thermally oxidized layers.
(1) M. Schoiswohl et al., Phys.Rev.B52,9889(1995) and Thin Solid Films 276, 92(1996)
- B-I/P16** **XPS CHARACTERIZATION OF STAIN-ETCHED POROUS SILICON FILMS**, R. Zanoni, Università di Roma "La Sapienza", G. Righini, CNR, Area della Ricerca di Roma, L. Schirone and G. Sotgiu, Università di Roma Tre, 00100 Roma, Italy
The surface composition and structure of freshly prepared as well as aged stain-etched porous silicon samples was investigated by X-Ray Photoelectron Spectroscopy (XPS). The presence of Si and Si oxide was revealed in all samples by the presence of two well-resolved Si2p components. Their binding energy separation is typical for Si (0) and SiO₂. A sol-gel structure for the Si oxide was suggested by the value of the Si Auger parameter. Small area and angle-dependent XPS measurements were carried out to check for samples homogeneity, within the photoelectron escape depth (3 nm for Si, in our experimental conditions). A nearly constant Si/SiO₂ atomic ratio was found in the lateral dimensions, and a small decrease with the depth. The presence of residual elements (C, N, F) from the preparation steps was investigated. Large variations in surface F was found. The XPS results of Si/SiO₂ atomic ratio at different photoelectron collection angles and Si Auger parameter, are compatible with a model for porous silicon layers in which Si grains are embedded in a SiO₂ thin matrix

- B-I/P17** MORPHOLOGY CONTROL OF STAIN ETCHED POROUS SILICON, L. Schirone, G. Sotgiu and F. Rallo, Università di Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy
In this work we investigated the relations among reflectance, morphology and preparation process of stain etched porous layers. The samples were characterised by means of reflectance spectrometry, and the results were fitted by a model, describing porous silicon as an effective medium consisting of air and crystalline silicon, with variable density throughout the film thickness. The deduced information on the film morphology provided a deeper insight on the relations among technological process, porosity profile and reflective properties. The films were used as Anti-Reflection (AR) and passivating coatings for large area, mono- and multi-crystalline silicon solar cells: an optimised design procedure is outlined, allowing to produce AR coatings with reflectance lower than 1.3% over the 350-1000nm wavelength range.
- B-I/P18** IN-SITU SURFACE-ROUGHNESS MEASUREMENTS DURING THE PREPARATION OF CHEMICALLY ETCHED POROUS SILICON, P.J. Harris, S.C. Bayliss, T. Bardrick, R. Hillman, R. Cubitt, Solid State Research Centre, De Montfort University, Leicester, UK
Porous silicon (PS) has been shown to exhibit an enhanced and shifted photoluminescence (PL) at room temperature. Although the subject of numerous research efforts worldwide the origin of this PL is still unknown. It is now generally accepted that quantum confinement of carriers within the nanocrystallites is probably responsible and hence the surface structure is of great importance. The chemical etch solution used in the preparation of stain-etched porous silicon consists of a mixture of hydrofluoric acid, nitric acid and water and the ratio of these components allows for some control of the final surface structure. However, the role each component plays in determining the final surface is not clearly understood. The corrosive nature of these etch solutions present an extremely hostile environment in general preventing in-situ analysis of the surface during the etch process. With a typical surface roughness of the order of nanometers, porous silicon has features on a scale that may be characterised by neutron reflectivity. Here we report neutron reflectivity measurements taken in-situ during the etch process. Etch times of up to 6 hours were employed and the resultant material showed a photoluminescent response in the red-orange.
- B-I/P19** VISIBLE LUMINESCENCE FROM PHOTO-CHEMICALLY ETCHED SILICON, N. Yamamoto and H. Takai, Takai Lab., Tokyo Denki University, 2-2 Kanda Nishikicyo, Chiyodaku, Tokyo 101, Japan
Porous silicon has been investigated widely because it can be formed easily by anodization of a single crystal silicon and exhibits visible luminescence at RT. In the anodization process, a constant current flow is required from the silicon (anode) to the counter-electrode (cathode) through a HF solution. However, it is difficult to apply the anodization process to SOI structure, such as SOS, because of a difficulty of the back contact formation. In this study, we will propose the photo-chemical etching method to form a visible luminescence layer on silicon, in which neither electrode nor current is required, and we will also discuss PL properties from the photo-chemically etched silicon. A single crystalline n-type Si wafer (100) having resistivity of 35-45 Ohm-cm was set at a bottom of the vessel filled with mixture of HF and H₂O₂ as an oxidant. He-Ne laser (633nm) is irradiated onto the Si wafer surface through the solution for photo-chemical reaction. Visible luminescence layer is formed selectively in the region the laser irradiated. Therefore formation of patterned visible luminescence layer on silicon wafer can be achieved. A photoluminescence (PL) of the photo-chemically etched layer is measured by a He-Cd laser (325nm) excitation. As a result, PL from photo-chemically etched layer has a peak wavelength at approximate 620nm and wide FWHM of approximate 0.3eV, and exhibits orange luminescence under daylight. The peak position and the wide FWHM from etched layer are similar to that from porous silicon. By dipping the layer in ethanol for 24 hours the luminescence color changes from orange to blue.
- B-I/P20** ANALYSIS OF GASES EVOLVED BY POROUS SILICON DURING ILLUMINATION IN DIFFERENT ATMOSPHERES, P. Martin, J.F. Fernandez and C. Sanchez, Dpto. Fisica de Materiales, Facultad de Ciencias, Universidad Autonoma de Madrid, Cantoblanco 28024 Madrid, Spain
Release of H from the surface of porous silicon after preparation or its oxidation change the PL characteristics. Silicon dangling bonds on the surface are initially passivated by H (or oxygen after oxidation) avoiding them to act as non-radiative centers. It has been reported that degradation of PL of PS is highly enhanced under illumination. Therefore, it is important to elucidate the nature of gases evolved by PS during, illumination with short enough wavelengths. To this purpose, silicon n-type wafers were used to prepare porous silicon. After preparation, PL of the sample was measured at room temperature in air and $\lambda=370$ nm excitation. Then, the sample was introduced in a camera where it was illuminated and the evolved gases analyzed with a mass spectrometer Quadstar 422 from Balzers. Influence of the light intensity and wavelength and composition of the atmosphere surrounding the sample has been investigated. Obtained results show a complex behaviour of the desorption process. In particular, no gas emission has been detected when the sample is in vacuum (10^{-7} mb) under illumination. Once the experiment has finished, the PL of the sample is again measured in order to compare it with the initial PL. (Supported by DGICYT, PB96-0084).
- B-I/P21** EFFICIENT LUMINESCENCE FROM POROUS SILICON, A. Daami, G. Bremond, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 Av. A. Einstein, 69621 Villeurbanne Cedex, France; J. Stalmans, J. Poortmans, IMEC, Kapeldreef 75, 3001 Leuven, Belgium
The observation of luminescence from porous silicon (PS) has initiated intensive research because of its potential for Si-integrated optoelectronics. However the poor time stability of this luminescence is still a major problem to be solved. The principal way of reducing the time-quenched luminescence is passivation of the dangling bonds of the crystallites formed inside the PS layer. In this work we present PL results of PS formed on both p-type Si substrates and diffused n⁺ emitters. First experiments reveal that photoluminescence (PL) from PS layers is enhanced after a passivation treatment with hydrofluoric acid (HF). Nevertheless the increase of the PL intensity is quickly lowered due to desorption of hydrogen because of the instability of Si-H_x bonds (ageing effect). Deposition of a nitride-layer on top of PS and PS nitridation have been investigated to passivate the PS luminescence. The nitride-deposition on PS mainly affects the PL-intensity through its anti-reflective behaviour in combination with a less pronounced ageing effect. However a significantly higher PL intensity as well as a stabilization in time have been observed in the case of the plasma-nitridation of PS. These observations are correlated to the higher stability of Si-N_x bonds.
- B-I/P22** ELECTROCHEMICAL BEHAVIOUR OF POROUS SILICON MULTI-LAYERS, R. Guerrero-Lemus, F.A. Ben-Hander, J.D. Moreno, R.J. Martin-Palma, J.M. Martinez-Duart, M.L. Marcos and J. Gonzalez-Velasco, Dpto de Fisica Aplicada and Dpto. de Quimica, C-IX, Univ. Autonoma de Madrid, 28049 Madrid, Spain; P. Gomez-Garrido, Dpto. Fisica Fundamental y Experimental, Univ. La Laguna, 38201 S/C de Tenerife, Spain
One of the problems to solve in order to achieve a porous silicon multilayer (PSM) is the accurate control of the thickness and porosity of the different superposed layers. In this work we have obtained two types of PSM's formed by alternate layers of high and low porosity with opposite order in each PSM. Both types of PSM's were submitted to anodic oxidation. The thicknesses of the different porous layers were measured by optical interferometry. The oxidation voltammograms recorded for each type of PSM present two different potential and time ranges which are related with the structure of the PSM's. The measurements of charge transfer in the oxidation voltammograms allow to deduce the total surface exposed to electrooxidation. Also, a qualitative study of the diffusion of the electrolyte in the formation process of the PSM's is exposed.

SYMPOSIUM B

- B-I/P23** DEPTH DEPENDENCE OF PHOTOLUMINESCENCE AND CHEMICAL BONDING IN POROUS SILICON, D. Dimova-Malinovska, M. Sendova-Vassileva, M. Kamenova, CL SENES, Bulg. Acad. Sci., 1784 Sofia, Bulgaria, and A. Kakanakova-Georgieva, Ts. Marinova, IGIC, Bulg. Acad. Sci., 1113 Sofia, Bulgaria
Porous silicon (PS) is studied by stepwise peeling of the surface layer to clarify the non-uniformity in the photoluminescence (PL) and correlate it with the in depth chemical bonding and structure of the 30 μm thick layer. The PL intensity grows by an order of magnitude after the peeling off of the first 10 μm and decreases five times in the next 5 μm while the peak maximum position shifts from 730 to 800 nm. XPS measurements show that Si-Si and Si-O bonds are present on the surface and in depth as well and the preferential oxidation state of silicon changes from 3+ and 4+ on the surface to 1+ and 2+ below 10 μm . Using Raman spectroscopy two different size distributions of silicon nanocrystals are shown to exist. The size of the smallest nanocrystals does not change with depth while that of the bigger nanocrystals grows. These results support the model relating PL to suboxide species present on the surface of PS.
- B-I/P24** LIGHT EMISSION FROM POROUS SILICON SUBJECTED TO DIFFERENT SURFACE TREATMENTS, N.I. Klyui, V.G. Litovchenko, A.G. Rozhin, A.B. Romanyuk, Institute of Semiconductor Physics, 45 prospect Nauki, 252028 Kiev, Ukraine; Y.P. Piryatinskii, Institute of Physics, 46 prospect Nauki, 252022 Kiev, Ukraine; V.A. Semenov, Institute for Superhard Materials, 2 Avtozavodskaya str., 254074 Kiev, Ukraine
Effect of different surface treatments such as rapid thermal annealing (RTA), rf plasma treatment, deposition of diamond-like carbon (DLC) films, and embedding of fullerene molecules into pores on porous Si (PS) properties was studied by time-resolved photoluminescence (PL). It was shown that rf (13.56 MHz) hydrogen plasma treatment enables the photoluminescence intensity of PS to be substantially increased. After deposition of DLC films the PL spectra both the PS and DLC are modified. Moreover, RTA of PS+DLC structure does not practically influence the PL band intensity, whereas the RTA of bare PS results in quenching of PS luminescence. Embedding of carbon clusters or fullerene molecules into pores of PS leads to sensibilisation of PS, fullerene and DLC luminescence.
- B-I/P25** A THEORETICAL MODEL OF THE PHOTOSENSITIVITY OF POROUS SILICON, B.S. Sokolovskii, Institute of Applied Physics of I. Franko State University, 290044 Lviv, Ukraine and L.S. Monastyrskii, I. Franko State University, 290005 Lviv, Ukraine
We have developed a new theoretical model of the photosensitivity of porous Si which takes into account the recombination of photocarriers at the surfaces of pores. The model is based on the processes of the carrier generation under illumination of the material, the ambipolar diffusion of carriers towards the internal surfaces, as well as the nonequilibrium carrier recombination in both the bulk of semiconductor and the surfaces of pores. By solving carrier transport equations with appropriate boundary conditions, the analytical relations for the photosensitivity of porous material have been obtained for the cases of the spherical and cylindrical shapes of pores. They describe the dependence of the porous Si photosensitivity on the mean sizes of pores and the distances between them, as well as on the surface recombination velocity. The photosensitivity of porous Si has been shown to decrease under increasing the porosity magnitude and the surface recombination velocity. The model developed may constitute a basis for an experimental method of determining the parameters of carrier recombination processes occurring at the internal surfaces of pores.
- B-I/P26** EFFECT OF OXYGEN IMPLANTATION ON IONOLUMINESCENCE OF POROUS SILICON, M. Kulik, T.J. Ochalski, J. Liskiewicz, J. Zuk, Institute of Physics, Maria Curie-Skłodowska University, Pl. Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland and A.P. Kobzev, Joint Institute of Nuclear Research, Dubna, Russia
Ionoluminescence (IL) presents an unique possibility to detect "in situ" optical emission during the interaction of ions with solids. Porous Si samples used in this study exhibited very weak visible photon emission after prolonged ambient air exposure. We implanted these PS layers with 225 keV O^+ ions at the dose of $1 \times 10^{17} \text{ cm}^{-2}$. Post-implantation annealing was subsequently performed in a flowing argon to restore Si crystalline order. Ionoluminescence was excited by 50 or 200 keV protons. The spectra are characterized by three band structures, increasing in intensity with the proton dose. Two of these bands (blue and red ones) have been observed in ionoluminescence of silica. The chemical composition of the porous Si samples, before and after O^+ implantation and annealing was investigated by Elastic Recoil Detection and Rutherford Backscattering with Nuclear Reaction methods. The results of this work show the important role of SiO_x defect related-states in oxygen implanted porous Si.
- B-I/P27** ELLIPSOMETRIC STUDY OF REFRACTIVE INDEX ANISOTROPY IN POROUS SILICON, H. Krzyzanowska, M. Kulik and J. Zuk, Institute of Physics, Maria Curie-Skłodowska University, Pl. Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland
Porous Si layers were produced by anodization of p^+ type (111) Si wafers. The porosity of these samples were in the range from 23% to 70 %. We used Multiple Angle of Incidence (MAI) ellipsometry at 632.8 nm to characterize optical anisotropy of porous silicon layers of prevailing wire-like morphology. Formulas for Fresnel's refraction coefficients, corresponding to uniaxially anisotropic film on an isotropic substrate, were used to determine ordinary and extraordinary refractive indices of porous Si layers. We assumed that values of extinction indices were negligible at this wavelength. For low porosities the porous Si layers can be described as cylindrical voids in crystalline Si. With the increasing of porosity a transition to Si wires on homogeneous substrate takes place. Both cases are included in theoretical models of the refractive index anisotropy.
- B-I/P28** RAMAN SCATTERING IN THICK FREE-STANDING POROUS SILICON FILMS, A.V. Andrianov and J. Morgan, Univ. of Nottingham, Department Electrical and Electronic Engineering, University Park, Nottingham NG7 2RD, UK; G. Polisski and F. Koch, Techn. Univ. Munich, Physics Department E-16, James-Frank-Strasse, 85747 Garching, Germany
We report the results of Raman scattering studies on free-standing porous Si layers with thickness up to 0.5 mm. The layers were created by electrochemical etching of both p- and n-type Si substrates in HF based solutions for times as long as 10 hours. To the best of our knowledge, the 0.5mm film is the thickest for free-standing porous Si layer achieved so far. The observed Raman spectra have a distinctive difference from experimental data previously reported either for porous Si films on Si substrates or for thin free-standing porous Si films. The spectra can not be directly fitted by the conventional phonon confinement model for Si-nanocrystals [1], which has been widely used for the interpretation of Raman scattering in porous silicon. The broadening of the observed Raman line is comparable in size with its downshift from the bulk Si Raman line. We believe that the observed discrepancies are caused by an existence of internal stress in these films. We have fitted our experimental data by a modified phonon confinement model that accounts for comprehensive stress. The comprehensive stress on the Si nanocrystals is a tensile one, with a value of $\sim 1-3 \text{ GPa}$ (estimated from this modified model). We have also made a X-ray diffraction investigation on these films. The X-ray data suggest the existence of tensile strain, whose magnitude is consistent with estimated stress in the thick free-standing films. The existence of this stress may also lead to the separation of the porous Si film from the substrate.
[1] I.H. Campbell and P.M. Fauchet, Solid State Commun., 58, 739 (1986)

- B-I/P29** EFFECT OF (STRESS) PREANNEALING OF Cz-Si SUBSTRATE ON PHOTOLUMINESCENCE OF POROUS SILICON, A. Misiuk, Institute of Electron Technology, Al. Lotnikow 46, 02 - 668 Warsaw, Poland; H.B. Surma, A. Brzozowski, A. Wnuk and M. Pawlowska, Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland

Porous silicon (PS) with red S - band photoluminescence (PL) was prepared by anodization of the p - type ($N_p = 2 \times 10^{15} \text{ cm}^{-3}$) Czochralski grown silicon (Cz-Si) with oxygen concentration up to above 10^{18} cm^{-3} in the 1:1 HF - isopropanol solution. Cz-Si was sequentially preannealed at 720 - 1620K for up to 40hrs at atmospheric or enhanced (up to 1.2GPa) pressure (HP) of argon. In effect of such treatment it were created different oxygen - related defects [1]. Properties of the Cz-Si substrate and of PS were determined by FTIR, SEM, TEM and X-ray methods. PL was excited by the Ar laser ($\lambda = 488 \text{ nm}$).

Between others, it were stated: a) marked dependence of the PS structure and of PL intensity on the conditions of preannealing, especially for the substrates with high concentration of oxygen - related defects, HP treated at above 1580K, with the PL shift from 700nm to 760nm, and b) appearance of the 640nm and 720nm PL components for PS prepared from the substrates with large oxygen precipitates created by preannealing at 720K and 1320K. Reported visible PL from HP - treated bulk Si [2] was not confirmed when using the Ar laser excitation.

[1] A. Misiuk, B. Surma, J. Hartwig, Mater. Sci. Eng. B36 (1996) 30;

[2] G.P. Karwasz et al., Appl. Phys. Lett. 69 (1996) 2900.

- B-I/P30** LUMINESCENTED PROPERTIES OF HYDROGENATED POROUS SILICON, V. Yerokhov, I. Melnyk, O. Iznin, Semiconductor Electronic Department, State University "Lviv Polytechnic", Box 1050, 290045 Lviv, Ukraine

The use of por-Si as the light emitter of the Si-based integrated optoelectronics requires improvement and stabilization of its luminescent properties. For it can be used the electrochemical hydrogenization of por-Si.

Current-potential potentiostatic curves of a system Pt(anode)-electrolyte-por-Si/Si for electrolytes with various chemical composition were read out for definition of por-Si electrochemical hydrogenization conditions with it cathode polarization. The spectra researching of its photoluminescence, before and after cathode polarization, was carried out for studying of an influence degree of an electrochemical hydrogenization on por-Si luminescent properties. The hydrogen saturation of por-Si surface during its cathode bias, increased a photoluminescence intensity up to a level, characteristic of samples, previously subjected to special chemical processing, is established.

Light Emission from Si: Author Approaches

- B-I/P31** INTRINSIC ELECTROLUMINESCENCE FROM In(III) OXIDE-Si HETEROSTRUCTURES AT ROOM TEMPERATURE IN STRONG INJECTION LEVEL CONDITIONS, A. Malik, E. Fortunato and R. Martins, CEMOP-UNINOVA/FCT-UNL, 2825 Monte de Caparica, Portugal

Due to the nature of the indirect bandgap structure, monocrystalline silicon has not been considered to be useful for light-emitting diodes. However, in the most pure Si with extremely well-passivated surfaces, as demonstrated by Yablonovitch et al [1], all the nonradiative processes can be virtually eliminated and internal quantum efficiency as high as 10% can be achieved. The aim of this work is to demonstrate a room-temperature electroluminescence (EL) at 1.075 eV from a light-emitting diodes based on heterostructures In(III) oxide-Si. The sample preparation does not require high-temperature furnace processings which might degrade the bulk carrier lifetime. The elimination of surface recombination was achieved both by chemical treatment of silicon surface in hot hydrogen peroxide solution and spray deposition technique for transparent conductive indium oxide electrode fabrication. Under these conditions, intensive electroluminescence at $T = 300 \text{ K}$ with an FWHM value of 60 meV have been obtained from diodes fabricated on high-quality n-type Si with resistivity of $10 \Omega \text{ cm}$ and lifetime nearly to 1 ms in a strong injection conditions (pulse current of 250-500 A/cm²). Both device fabrication aspects and its electrophysical and EL characteristics will be discussed.

[1] E. Yablonovitch and T. Gmitter, Appl. Phys. Lett. 49 (1986) p. 587.

- B-I/P32** ELECTROLUMINESCENCE FROM Si-Si_{1-x}Ge_x/Si_{1-y}C_y-Si p-i-n DIODES STRUCTURES, K.B. Joelsson, W.-X. Ni, G. Pozina, C.-X. Du, G.V. Hansson, Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden

Enhanced no-phonon radiative recombination at wavelengths up to 1.3 μm has been obtained in electroluminescence by interfacial recombination in Si-Si_{1-x}Ge_x/Si_{1-y}C_y-Si p-i-n diodes ($x \approx 15\%$ and $y \approx 2\%$). For high current injection the interfacial recombination is dominant. Under other conditions, i.e., low current injection and at low temperature radiative recombination in the Si_{1-x}Ge_x layer may be dominant. The interface-related emission consists of two peaks; one no-phonon (NP) and one peak that is assigned as a phonon replica. For the emission peaks associated with the radiative recombination occurring at the interface, the NP peak is more intense, while for the peaks associated with recombination occurring in the Si_{1-x}Ge_x layer, phonon-assisted emission is more intense. For the up to now studied structures, Si band-to-band recombination is observed for temperatures higher than 250K. The p-i-n diode structures have been processed both for normal and edge-emitting geometries.

- B-I/P33** PHOTOLUMINESCENCE AND X-RAY CHARACTERIZATION OF Si/Si_{1-x}Ge_x MULTIPLE QUANTUM WELLS, T.P. Sidiki, A. Rühm*, W.-X. Ni**, G.V. Hansson**, C.M. Sotomayor Torres, Institut für Materialwissenschaften, Fachbereich Elektrotechnik, BUGH Wuppertal, 42097 Wuppertal, Germany, *Institut für Materialwissenschaften, Fachbereich Physik, BUGH Wuppertal, 42285 Wuppertal, Germany, **Department of Physics, Linköping University, 581 83 Linköping, Sweden

Recently Miyao et al. [1] have reported on a strongly reduced PL intensity due to clustering of Ge atoms which is most striking for temperatures between 400°C and 650°C. Here we present a combined photoluminescence and x-ray diffraction study of two SiGe multiple quantum well samples grown at 600°C and 650°C, respectively. Temperature, power and wavelength dependent photoluminescence experiments were performed. An enhanced PL yield and an increased quenching temperature were observed for the sample grown at the higher temperature. X-ray diffraction revealed high Ge concentration fluctuations within the SiGe layers and rougher Si/SiGe interfaces due to Ge segregation at the higher growth temperature. However, neither the Ge clustering nor the interface roughness appeared to affect the luminescence increase. These could be attributed to less vacancies, less point defects and less Sb incorporation within the Si_{1-x}Ge_x layers grown at the higher temperature. More experiments are in progress.

[1] M. Miyao, K. Nakagawa, Y. Kimura, and M. Hirao, Thin Solid Films 294, 204 (1997)

- B-I/P34** SHORT PERIOD (Si₆Ge₄)_p SUPERLATTICES: PHOTOLUMINESCENCE AND ELECTRON MICROSCOPY STUDY, N. Pinto, M. De Crescenzi, R. Murri, F. Tombolini, INFN Dipartimento di Matematica Fisica, Università di Camerino, 62032 Camerino, Italy; M. Casalbani, INFN Dipartimento di Fisica, Università di Roma Tor Vergata, Roma, Italy; G. Barucca, G. Majni, INFN Dipartimento di Scienze della Terra e dei Materiali - Università di Ancona, Ancona, Italy

High quality (Si₆Ge₄)_p heterostructures, fully strained on Si (100) substrates, have been investigated by photoluminescence (PL) measurements. The films were grown by molecular beam epitaxy using Sb as surfactant. The spectra have been obtained as a function of the progressive increasing repetition number (P). The PL results of the whole set of samples show similar spectra, for both the single Ge quantum well (P=1) and the thicker heterostructure (P=30). The features of these spectra revealed that excitonic recombination occurs in the Ge layers and it is indirect in nature, whatever the structure (P) was. These results suggest a high localization in the PL process excluding any superperiodicity effect.

Transmission electron microscopy (TEM) investigation evidenced both a high crystallographic structures and the absence of any defects.

- B-I/P35** **VISBLE PHOTOLUMINESCENCE FROM a-Si/SiO₂ SUPERLATTICES FABRICATED BY UHV EVAPORATION**, K. Nishimoto, H.A. Durand, K. Etoh, K. Ito, Japan Aviation Electronics Industry Ltd, Central Research Laboratory, Musashino 3-1-1, Akishima-shi, Tokyo 196-8555, Japan
In the search for a light source compatible with Si technology for optoelectronic and display devices, we have fabricated a-Si/SiO₂ superlattices by UHV evaporation. This method enables an accurate control of each layer's thickness as confirmed by XRD and TEM. PL and PLE spectra of our samples show two prominent emission bands centered at 1.65eV (I-band) and 1.82eV (II-band). We studied the behaviours of these two bands as a function of temperature between 3 and 300 K and as a function of excitation power; these responses are very distinct. According to the peak intensity variation of I-band with excitation power, it is likely due to interface emission, in the same way as it has been reported for porous Si*. In contrast, II-band shifts towards higher energies when excitation power is increased and can not be attributed to the same mechanism. Moreover, we investigated further a mechanism for II-band, and the role of quantum efficiency for our samples.
*K.Murayama et. al, Jap. J. Appl. Phys., Vol. 31 (1992) pp L1358-L1361
- B-I/P36** **MULTIPERIOD Si/SiO₂/Ge LAYERED STRUCTURE FORMATION THROUGH CHEMICAL BOND MANIPULATION**, K. Prabhakaran, T. Ogino, NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan, and T. Matsumoto, Y. Masumoto, Single Quantum Dot Project, ERATO, JST, 5-9-9 Tohkohdai, Tsukuba, Japan
In the emerging area of fabrication of nanostructured materials, control of atomic processes is a key approach to achieving the formation of the desired species. Nanostructure formation through self-organization process is more preferred over other methods due to the possibility of wafer scale integration. Chemical bond manipulation, we present here, is a self-organization process and involves controlled breaking and making of bonds, thereby enabling the formation of the desired species on a full wafer scale. An ultrathin layer of Ge (0.65 nm) was deposited on a Si(111) substrate and oxidized. On depositing Si (2 nm - 3 nm) onto this surface at room temperature, Ge-O bonds are broken and results in the formation of ultrathin SiO₂ (~1 nm) capped by ultrathin Si (1 nm - 2 nm). The processes were repeated several times and resulted in the formation of multilayer structure of ultrathin Si and Ge layers sandwiched between ultrathin SiO₂. Photoelectron spectroscopy results confirm the breaking of Ge-O bonds and formation of Si-O in each layer. Most interestingly, this new material is found to emit blue-green light when excited by ultra-violet laser.
- B-I/P37** **STRONG VISIBLE PHOTOLUMINESCENCE IN AMORPHOUS SiO_x:H PREPARED BY THERMAL EVAPORATION OF SiO POWDER**, H. Rinnert, M. Vergnat, G. Marchal, Laboratoire de Physique des Matériaux, (U.M.R. au C.N.R.S. No.7556), Université Henri Poincaré Nancy 1, B.P. 239, 54506 Vandoeuvre-lès-Nancy Cedex, France; A. Burneau, Laboratoire de Chimie Physique pour l'Environnement, (U.M.R. au C.N.R.S. No.7564), Université Henri Poincaré Nancy 1, 405 rue de Vandoeuvre, 54506 Villers-lès-Nancy Cedex, France
Amorphous SiO_x films were elaborated by thermal evaporation of SiO powder under a flow of hydrogen ions onto silicon substrates maintained at 100 °C. Photoluminescence (PL) can be seen in the visible range at the naked eye on the as-deposited samples without post-treatments. Annealing treatments were performed to understand the role of hydrogen and oxygen on the PL properties. Hydrogen and oxygen bonding was studied by infrared spectrometry and hydrogen effusion was followed by thermal desorption spectrometry experiments. With increasing annealing temperature, a continuous red shift of the PL was observed. However the PL intensity first increased for temperature inferior to 650 °C and then decreased for further annealing temperature. Both infrared Si-O-Si stretching mode peak shift and PL peak shift demonstrated the material is not an homogeneous film but contains oxygen rich regions and silicon rich regions. Both shift and intensity of the PL peak can be explained by a model of growth and coalescence phenomenon of Si rich regions. The PL is attributed to the quantum confinement of excitons in a-Si clusters embedded in the SiO_x matrix. The hydrogen content of films does not correlate with the PL intensity and the most efficient sample contains hardly any hydrogen. Our results demonstrate oxygen creates an efficient potential barrier and no further passivation by hydrogen is necessary.
- B-I/P38** **VISIBLE PHOTOLUMINESCENCE AND IT'S MECHANISM FROM DEFERENT STOICHIOMETRIC a-SiO_x:H THIN FILMS**, M. Zhu, Graduate School, Academia Sinica, PO Box 3908, Beijing, China; R.B. Wehrspohn, Lab. PMC, Ecole Polytechnique, 91128 Palaiseau, France and C. Godet, Lab. PICM, Ecole Polytechnique, 91128 Palaiseau, France
The three commonly reported photoluminescence (PL) bands centered around 1.7 eV, 2.1 eV and 2.9 eV have been observed from a-SiO_x:H thin films with different oxygen contents (x = 1.35, 1.65 and 2). The 1.7 eV line shows a significant thermal quenching of the PL intensity, which is consistent with the model of tail-to-tail state transitions in a-Si. In contrast, no temperature quenching of the 2.1 eV and 2.9 eV PL was observed. Gas evolution and infrared data show that an increase in the intensity of 2.1 eV PL is accompanied by a decrease in hydrogen content after annealing at 400 °C. For the films annealed to > 400 °C, the 2.1 eV PL intensity decreases with T and opposite behavior was measured for the Si-O-Si vibration intensity. The initial increase and the following decrease of the 2.1 eV PL intensity were discussed by microscopic defect reactions and further explained by oxygen vacancy defect model. A strong correlation of the 2.9 eV PL intensity and the H-O-Si infrared signal was observed upon annealing the sample from 400°C to 900°C. The radiative defects associated with H-O-Si groups are probably responsible for the 2.9 eV light emission.
- B-I/P39** **ROOM TEMPERATURE VISIBLE PHOTOLUMINESCENCE FROM Ar⁺- AND Ge⁺-ION IMPLANTED Si₃N₄ AND SiO_xN_y FILMS**, I.E. Tyschenko, G.A. Kachurin, Institute of Semiconductor Physics, Novosibirsk, 630090, Russia; L. Rebohle, W. Skorupa, Institute of Ion Beam Physics and Materials Research, Research Center Rossendorf, Inc. POB 510119, 01314 Dresden, Germany
Room temperature photoluminescence (PL) emission and excitation spectra from Ar⁺- and Ge⁺-ion implanted SiO_xN_y (x=0.25, y=1) and Si₃N₄ films were investigated as a function of ion dose and annealing temperature. It was found that both Ar⁺- and Ge⁺-ion implantation into these films led to the formation of green-yellow PL band around 520 nm. Further increase in the ion dose caused PL to decrease. The PL intensity dependence on the annealing temperature was found to be different for different excitation wavelengths. In the case of SiO_xN_y-films, PL intensity excited with the wavelength of 320 nm grew with increase in annealing temperature up to 1000°C. For the excitation wavelengths longer than 360 nm, maximum PL intensity was achieved after annealing at 600°C. The behaviour of PL spectra observed from Ge⁺-ion implanted Si₃N₄ was similar to that from SiO_xN_y films. However, Ar⁺-ion implanted Si₃N₄ layers showed green-yellow PL band with the intensity of 20-30 times higher than that from Ge⁺-ion implanted Si₃N₄ and SiO_xN_y films. The nature of light emitting centres is discussed and associated with Si- SiN_x clusters formed by ion implantation and with their subsequent annealing in the nitride and oxynitride matrices.
- B-I/P40** **XPS INVESTIGATION OF a-Si:H THIN FILMS AFTER LIGHT SOAKING**, A. Toneva, T. Marinova* and V. Krastev*, Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria; *Institut of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
Amorphous hydrogenated silicon thin films prepared by homogeneous chemical vapour deposition have been studied. The Si2p, O1s and C1s electron spectra have been recorded for different light soaking times using repeated 100 mW/cm² white light illumination and X-ray photoelectron spectroscopy (XPS) measurements. The change of the position and intensity of the Si2p peak has been observed after light soaking, which is explained by the transformation of the Si-H bonds. The correlation between micropore density in a-Si:H film and the Si2p peak behaviour is demonstrated.

B-I/P41 LIGHT EMISSION FROM SILICON P-N JUNCTION AT AVALANCHE AND SECONDARY BREAKDOWN, T. Puritis, J. Kaupuzs, Riga Technical University, Lab. of Semicond. Phys., 1a Kalku str., 1658 Riga, Latvia

Up to now it is considered that light emission is caused by electron indirect transitions from the first conduction band to heavy hole band (c-v transitions) at avalanche breakdown. It is contradiction with two experimental results. It is showed [1] that impact ionization initiate "light" charge carriers in silicon. It means that bands of light charge carriers are populated and direct transitions from the second conduction band to the first (c-c transitions) are possible. Recently Canali a. o. [2] computed spectral distribution of light caused by direct c-c transitions and they established good accordance with experimental ones. Experimental distribution reported in [3] are compared with Canali's a. o. theoretical ones. It is concluded that light emission is related with direct c-c transition at premesoplasma and partial with mesoplasma (at secondary breakdown), too. The shape of a space distribution of mesoplasma emission are calculated in profile. It is concluded that mesoplasma emission is related with direct c-c transitions in central region of mesoplasma and with indirect c-v transitions in periphery.

[1] T. Puritis. Microelectr. Reliab., 1997, 37, 713.

[2] L. Carbone a.o. Semicond.Sci.Techn., 1994, 9, 674.

[3] V. Eglitis a.o. Latvian J. Phys.Techn.Sci., 1970, 6, 58.

B-I/P42 ELECTRONIC, OPTICAL AND TRANSPORT PROPERTIES OF SEMICONDUCTING IRON DISILICIDE, A.B. Filonov, V.E. Borisenko, Belarusian State University of Informatics and Radioelectronics, P. Browka 6, 220027 Minsk, Belarus and W. Henrion, H. Lange, Hahn-Meitner Institut, Rudower Chaussee 5, 12489 Berlin, Germany

This is a review of recent theoretical and experimental results obtained for β -FeSi₂. Electronic structure calculations performed by *ab initio* LMTO method within the LDA scheme including exchange and correlation effects have shown the existence of *quasi-direct* band gap structure in the material. It is experimentally confirmed that between the threshold energy of optical interband transition of 0.73 eV and the first direct gap transition with appreciable oscillator strength at about 0.87 eV there is a region in which direct transition of low oscillator strength and indirect transitions overlap.

The interband optical spectra of β -FeSi₂ were investigated in the energy range from 0.5 to 5.0 eV. The dielectric and other optical functions were simulated and deduced from ellipsometry experiments. Reasonable agreement between the calculated and measured data has been obtained.

Estimations of mobility versus temperature for β -FeSi₂ in relaxation time approximation have been performed. A power-law temperature dependence $T^{-\alpha}$ with $\alpha > 3/2$ in high-temperature region can be obtained with inclusion of acoustic and nonpolar phonon scattering. The results obtained have shown the minor influence of polar optical phonon scattering. The power of the exponent is strictly affected by neutral impurity scattering which mainly relates to the purity of the material.

Thursday June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-Midi

Poster Session II
16:30-19:00

Nanocrystals

- B-II/P1** THE ORIGIN OF BLUE AND RED LUMINESCENCE IN Si NANOCRYSTALS GROWN BY ION-IMPLANTATION, S. Guha, Naval Research Laboratory, Washington DC, USA
Two photoluminescence (PL) bands, one in the blue (420 nm) and the other in the red (780 nm), have been observed in the annealed (900 °C) samples of Si implanted in thermally oxidized Si. An excitation wavelength dependence of these two PL bands has been conducted to determine their origin. The red band was found to shift as a function of excitation wavelength, while the blue band remains fixed in position. This observation leads us to believe that the red band is associated with Si nanocrystals, while the blue band is associated with non-paramagnetic defects in the oxide matrix. From the observed blue shift of the red band as a function of excitation wavelength, we determine a band gap distribution that arises due to the size distribution of Si nanocrystals. Our TEM measurements indicate a size distribution of Si nanocrystals between 2 and 6 nm.
- B-II/P2** PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE INVESTIGATIONS AT Ge-RICH SiO₂ LAYERS, L. Rebohle, J. von Borany, I.E. Tyschenko, W. Skorupa, FZ Rossendorf e.V., Dresden, Germany; H. Fröb, TU Dresden, Germany
Strong blue and violet photo-PL and electroluminescence (EL) at room temperature was obtained from SiO₂-films grown on crystalline Si, which were implanted with Ge ions and annealed at different temperatures. The PL spectra of Ge-rich layers reach a maximum after annealing at about 600°C. Both PL and EL intensities of 500 nm thick Ge-rich layers are easily visible by the naked eye at ambient light. Based on excitation spectra we tentatively interpret the blue PL as due to the oxygen vacancy in silicon dioxide. Electrical and EL measurements were carried out at MOS capacitors using an transparent ITO and a thick Al front contact, respectively. The electrical properties of the oxide and the SiO₂-Si-interface were investigated by C-V and I-V-measurements. The I-V-dependence exhibiting the typical behaviour of Fowler-Nordheim tunneling shows an increase of the break-down voltage and the tunneling current for Ge-rich oxide in comparison to the unimplanted material. The EL spectrum of the Ge-implanted oxide correlates very well with the PL one and shows a linear dependence on the injected current over three orders of magnitude. EL efficiencies in the order of 10⁻⁴ for Ge⁺-implanted silicon dioxide were determined.
- B-II/P3** THE EFFECT OF ANNEALING UNDER HYDROSTATIC PRESSURE ON THE VISIBLE PHOTOLUMINESCENCE FROM Si⁺-ION IMPLANTED SiO₂ FILMS, I.E. Tyschenko, G.A. Kachurin, Institute of Semiconductor Physics, Novosibirsk, 630090, Russia, A. Misiuk, Institute of Electron Technology, Al.Lotnikow 46, Warsaw, Poland, L. Rebohle, W. Skorupa, Institute of Ion Beam Physics and Materials Research, Research Center Rossendorf, Inc. POB 510119, 01314 Dresden, Germany
The effect of annealing under hydrostatic pressure on the photoluminescence (PL) from thermally grown SiO₂ films implanted with Si⁺ ions was investigated. Silicon ions were implanted at the double energy of 100 and 200 keV to doses of 3.9x10¹⁶ and 6.3x10¹⁶ cm⁻², respectively. The substrate temperature during implantation was maintained at about -155...-140°C. Subsequent annealing was carried out at the temperature of 400-1130°C in argon atmosphere under hydrostatic pressure of 1 bar - 15 kbar. Room temperature PL was excited with the wavelengths of λ_{ex} =250 and 514 nm. For λ_{ex} =250 nm, high intensity blue PL peaking at 460 nm and broad orange PL band of much reduced intensity around 600 nm were observed from the 450°C annealed layers. It was found that the intensity of both blue and orange PL bands increased as a log function of pressure. For λ_{ex} =514 nm, the near-IR PL band (around 800 nm) was observed from the layers annealed without pressure. The anneal under pressure led to vanishing of this band. The mechanism of hydrostatic pressure annealing effect on the light-emitting centers formation is discussed.
- B-II/P4** EXCESS Si CONCENTRATION DEPENDENCE OF THE PHOTO-LUMINESCENCE OF Si NANOCCLUSERS IN SiO₂ FABRICATED BY ION IMPLANTATION, T. Shimizu-Iwayama, Aichi University of Education, Igaya-cho, Kariya-shi, Aichi 448-8542, Japan and D.E. Hole, P.D. Townsend, University of Sussex, Brighton BN1 9QH, UK
A novel method for the fabrication of luminescent Si nanoclusters in an amorphous SiO₂ matrix by ion implantation is reported. We have measured dose (excess Si concentration) and annealing time dependence of the photoluminescence of Si nanoclusters in Si O₂ layers at room temperature. The samples were fabricated by ion implantation and subsequent annealing at 1050 °C. After annealing, a photoluminescence band peaked below 1.7 eV has been observed. The peak energy of the photoluminescence is found to be independent of annealing time, while the intensity of the luminescence increases as the annealing time increases. Moreover, we found that the peak energy of the luminescence is strongly affected by dose of implanted Si ions especially in the high dose range (high excess Si concentration). These results indicate that the photons are absorbed by Si nanoclusters, for which the band-gap energy is modified by the quantum confinement effects, and the emission is not simply due to direct electron-hole recombination inside Si nanoclusters, but is related to defects probably at the interface between Si nanoclusters and Si O₂, for which the energy state is affected by Si cluster-cluster interactions. It seems that the Si nanoclusters react via a thin oxide interface and the local concentrations of Si nanoclusters play an important role in the peak energy of the photoluminescence.
- B-II/P5** DEPENDENCE ON SUBSTRATE TEMPERATURE OF EFFICIENCY OF CO-SPUTTERED Si/SiO₂ LAYERS, S. Charvet, R. Madelon B. Rizk, LERMAT, unité CNRS 6004, 6 Bd Maréchal Juin, 14050 Caen cedex, France, and B. Garrido, O. Gonzalez, M. Lopez, A. Pérez-Rodríguez, J.R. Morante, EME, Departament d'Electronica, Universitat de Barcelona, Avda Diagonal 645-647, 08028 Barcelona, Spain
Si nanograins were thermally grown in a SiO₂ matrix after deposition by magnetron sputtering at substrate temperatures (T_s) varying from 200°C to 700°C. The structural and optical characteristics were investigated by infrared absorption (IR), Raman scattering (RS) and X-Ray photoelectron spectroscopy (XPS), in addition to photoluminescence (PL) techniques. Intense deep red PL (820 nm) was detected for samples deposited at T_s=500°C. At this temperature, complete phase separation is observed. RS shows a high degree of Si crystallization into nanograins and at same time IR shows a tendency of the matrix towards stoichiometric SiO₂. The IR results also suggest an abrupt Si/SiO₂ interface. The XPS results demonstrate that silicon incorporation is maximized at this temperature. For other temperatures, PL emission drops and shifts towards the red visible spectrum (740 nm). This shift is likely due to the existence of a-Si domains as revealed from RS while no crystalline silicon is detected. The results have been interpreted in terms of the influence of silicon incorporation in the improvement of phase separation and crystallization. A reduction of interface non-radiative states for abrupt interfaces are expected to lead to the observed enhancement of the PL efficiency.

- B-II/P6** PHOTOLUMINESCENCE OF Ge NANOSTRUCTURES GROWN BY MBE ON SILICON (118) SUBSTRATE, M. Serpentine, G. Bremond, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 Av. A. Einstein, 69621 Villeurbanne Cedex, France; M. Abdallah, I. Berbezier, CRMC2-CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France

Quantum dots are expected to give a significant quantum efficiency enough to be applied in Si-based optoelectronic devices used in the spectral range of interest for telecommunications 1.3-1.6 μm . The aim is to control island growth and self-organisation growth seems to be a promising method to obtain 0D confinement.

In this work, we propose a photoluminescence analysis of Si/Ge/SiGe/Si structures grown on a non conventional Si (118) substrate at 550°C by MBE. Indeed, a SiGe wetting layer grown on a silicon (118) substrate exhibits undulations and the Ge monolayers are grown on these undulations according to the Stranski-Krastanov mode. First, low temperature photoluminescence spectra obtained with variable Ge thickness, show the changeover 2D-3D growth mode and islands-related luminescence is observed up to room temperature. Moreover, the comparison between two samples respectively grown with and without wetting layer reveals that growing a wetting layer induces a better dot size homogeneity. Second, we found an important shift of the peaks towards higher energies when increasing the power excitation. So, we presume that the dots related transition is likely a type II transition and we will discuss this opinion referring to precedent results and time resolved PL measurements.

- B-II/P7** ROOM TEMPERATURE VISIBLE PHOTOLUMINESCENCE FROM CRYSTALLIZED NANO-Si THIN FILMS, Wei Wu, J.B. Xu, Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong; M.X. Wang, X.F. Huang, K.J. Chen, W. Li, J. Xu, Department of Physics, Nanjing University, Nanjing 210093, China
- Room temperature visible light emission was observed from 20 nm thick Si nanocrystalline layer, which is deposited on quartz substrate by plasma enhanced chemical vapor deposition (PECVD) system and subsequently irradiated by KrF excimer laser through an optical grating. Atomic force microscope (AFM) revealed the formation of self-organized Si nanocrystallites in laser irradiation region, with measured grain size of about ten nanometers. Room temperature visible photoluminescence (PL) was observed both from crystallized sample and the sample with subsequent hydrogen plasma annealing, two peak wavelength at 580 and 700 nm were shown. Morphologies and PL peak intensities were changed after H plasma annealing. Considering the luminescent characteristics and sample structures, we speculate the prepared Si nanocrystallites, which is small enough to quantize the electronic states, lead to a large increase of the effective band gap and a more efficient radiative recombination. In addition, hydrogen related species also have contributions on the light emission.

- B-II/P8** THE MECHANISM OF THE INTRINSIC 'RED' PHOTOLUMINESCENCE FROM nc-Si/SiO₂ THIN FILMS, S. Veprek, T. Wirschem, Ch. Ossadnik, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, 85747 Garching, Germany and S.M. Prokes, W.E. Carlos, Naval Research Laboratory, Washington D.C. 20375, USA

The PL mechanism from nc-Si/a-SiO₂ thin films with a controllably varied crystallite size from 10 to 1.5 nm and their separation (0.3 to ≥ 2 nm) was investigated by means of a number of techniques including, among others, spectral distribution and its dependence on the crystallite size and power of the excitation light, decay time, polarization measurements, PL-excitation spectra, microwave absorption due to the photogenerated carriers and electron spin resonance, ESR. Various PL-features frequently observed and reported could be attributed to impurities or defects in the SiO₂ and excluded as intrinsic PL from nc-Si/a-SiO₂. The results of these investigation provide a consistent mechanism of the intrinsic 'red' PL which consists of a broad feature with a maximum between about 1.5 and 1.7 eV. Accordingly, the photogeneration of the electron-hole pairs occurs within the Si-nanocrystals and shows the behavior expected from the quantum confinement model (increase of the band gap and photogeneration rate with decreasing crystallite size). These e-h pairs are quickly trapped at the Si/SiO₂ interface from which the PL occurs. The ESR measurements show a clear correlation of the PL intensity with the ESR-signal from thermal donors consisting of clusters of non-bridging oxygen hole centers (NBOHC). These centers are found only in nc-Si/SiO₂ samples which show the PL. They are absent in nc-Si films which have not been passivated by the SiO₂ and thus show no PL.

- B-II/P9** CATHODOLUMINESCENCE PROPERTIES OF SILICON NANOCRYSTALLITES EMBEDDED IN SILICON OXIDE THIN FILMS, T. Inokuma, Y. Kurata and S. Hasegawa, Dept. of Electrical & Computer Engineering, Faculty of Engineering, Kanazawa Univ., 2-40-20 Kodatsuno, Kanazawa 920, Japan

Recently, we have demonstrated that silicon suboxide films subjected to high-temperature annealing exhibit an efficient photoluminescence (PL) and that Si nanocrystallites are formed in the films [T. Inokuma et al., J. Appl. Phys. 83, 2228 (1998)]. The chemical stability and robustness of those films promise their high suitability for electronic and optic device applications. In this contribution, we focus on luminescence properties due to electron injection for the Si nanocrystallites embedded in a matrix of silicon oxide films, using a cathodoluminescence (CL) technique.

The CL spectra observed for the samples composed of two principal bands whose peak energies are in a near-infrared (NIR) region (~ 1.6 eV) and in a blue region (~ 2.6 eV), respectively. The spectral feature of the NIR CL bands is similar to the PL spectra under an excitation light of 2.54 eV. The strong correlation between the presence of Si nanocrystallites and the formation of the NIR CL band are found as well as the PL spectrum. The peak energy of the blue CL band is close to that of the luminescence band originates from oxygen vacancies in SiO₂. Therefore, the blue CL band is considered to come from the oxide matrix. Under irradiation of electron beams, degradation of the intensity is observed for both the CL bands but the decay characteristics for the two bands are different. Effects of hot electron injection on the luminescence properties will be discussed on the basis of the CL results for the samples prepared with various conditions.

- B-II/P10** LIGHT EMISSION FROM NANOCRYSTAL Si EMBEDDED IN CaF₂ EPILAYERS ON Si (111): EFFECT OF RAPID THERMAL ANNEALING, M. Watanabe, T. Maruyama, S. Ikeda, Research Center for Quantum Effect Electronics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Room temperature visible photoluminescence (PL) of nanocrystal silicon (nc-Si) embedded in single crystal CaF₂ formed on Si(111) has been demonstrated and the influence of rapid thermal annealing (RTA) on the PL spectra has been studied.

Recently, we have demonstrated formation of nc-Si in CaF₂ epilayers on Si(111) and reported visible PL at temperature range from 20K to room temperature. However, at room temperature, PL intensity was relatively weak and inhomogeneous. In this paper, we have introduced *ex-situ* rapid thermal annealing (RTA) process for nc-Si/CaF₂ and have found that PL intensity and uniformity was improved by RTA with appropriate temperature and annealing time.

Nc-Si embedded in a CaF₂ epilayer was prepared by coevaporation of Si and CaF₂ flux in ultra high vacuum ($<1 \times 10^{-9}$ Torr) on Si(111) substrate. Nc-Si with diameter less than 10nm can be obtained under the appropriate flux ratio (Si:CaF₂=1:1-1:5) and growth temperature (30-300°C). After the growth, *ex-situ* RTA was performed in H₂ or N₂ at temperature range from 750-1050°C for annealing time of 10-1000sec. We have found that RTA at around 750°C for about 10sec results in improvement of PL intensity and uniformity, however, temperature higher than 950°C and longer annealing time leads to degradation of surface morphology and PL intensity with drastic change of PL spectra.

- B-II/P11** ELLIPSO-METRIC SPECTROSCOPY STUDY OF PHOTOLUMINESCENT Si/SiO₂ SYSTEMS OBTAINED BY MAGNETRON CO-SPUTTERING, S. Charvet, R. Madelon, F. Gourbilleau, R. Rizk, LERMAT, Unité CNRS 6004, 6 Bd du Maréchal Juin, 14050 Caen cedex, France
The Si nanograins embedded in SiO₂ tissue, grown by thermal annealing after deposition by magnetron co-sputtering, were found to be the center of room temperature photoluminescence (PL) in the visible range. Beside the PL measurements, these structures were analyzed, before and after annealing, by infrared absorption (IR) and high-resolution electron microscopy (HREM), in addition to a careful analysis by ellipsometric spectroscopy (ES) techniques. The evolution of the PL efficiency with the deposition temperature (T_d) showed a maximum for T_d=500°C, which was correlated to the trend of the matrix of this sample toward stoichiometric SiO₂, as indicated by the IR data. These results are corroborated by the HREM observations that show evidence of the formation in this sample of Si nanocrystallites of about 3 nm. The ES measurements performed between 1.5 and 4.2 eV revealed a noticeable decrease, upon annealing, of the imaginary part of the dielectric function ϵ_2 . The decrease of ϵ_2 values is more important for T_d lying between 400° and 500°C, i.e. that corresponding to the most crystallized and photoluminescent sample. These results were interpreted on the basis of the increasingly important phase separation for the higher PL, as suggested by the increasing shift of the ϵ_2 values towards those relating to SiO₂. This would also imply a decrease of the Si/SiO₂ interface defects.
- B-II/P12** LOCALIZED ELECTRON STATES INDUCED BY DOPING AMORPHOUS SILICON, G. Allan, C. Delerue, M. Lannoo, Institut Supérieur d'Electronique et de Microélectronique du Nord, Département ISEN, BP 69, 59652 Villeneuve d'Ascq Cedex, France
The electronic structure of doped bulk amorphous silicon and nanoclusters is calculated within the tight-binding approximation. Using the Wooten-Winer-Weaire model [1] we calculate the localized electron band tails due to hydrogenic impurities in hydrogenated material. Contrary to bulk crystalline silicon, hydrogenic impurities give rise to deep levels. This leads to quite large impurity binding energies which can be equal to a few tenths of eV. Such values arise for electronic states with small spatial extension close to the impurity. We also show that these tails strongly depend on the nature of the impurity. We analyse the consequences of the doping on the luminescence of bulk material and amorphous silicon clusters. The results are compared to the experimental values for amorphous porous silicon.
[1] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. 54, 1392 (1985); F. Wooten, and D. Weaire, Solid State Phys. 40, 1 (1987); B. R. Djordjevic, M.F. Thorpe, and F. Wooten, Phys. Rev. B 52, 5685 (1995).
- B-II/P13** A LIGHT EMITTING DIODE STRUCTURE BASED ON Si NANOCRYSTALS FORMED BY IMPLANTATION INTO THERMAL OXIDE, N. Lalic and J. Linnros, Department of Electronics, Royal Institute of Technology, Electrum 229, 164 40 Kista-Stockholm, Sweden
Light emitting diodes have been produced by implantation of Si into SiO₂. On the p-type Si wafers, thermal oxide with thickness between 120 Å and 1000 Å was grown and a 2000 Å thick amorphous Si layer was deposited on top of the oxide. Into this structure Si ions were implanted with the energy of 150 keV. The structure was then annealed at 1100 °C in order to form nanocrystallites in the oxide and to crystallize the amorphous Si layer. Finally, n-type contact pads were created by the deposition of a 1600 Å thick polysilicon layer, in situ doped with phosphorus. This diode structure has shown rectifying behaviour, with a rectifying factor of ~ 10 at 10 V. Room-temperature electroluminescence (EL) was observed both under forward and reverse polarization in air ambient. Under forward polarization, EL was considerably stronger and the EL rise and fall time constants were under 10 µs. Continuous and pulsed operation was possible, depending on the oxide layer thickness. In the case of pulsed operation, duty cycle was up to 0.5. No fatiguing has been observed in either mode of operation.
- B-II/P14** LIGHT EMISSION FROM NANOSTRUCTURED SILICON FILMS PRODUCED BY PULSED LASER ABLATION, O.F. Bobrenok, A.V. Bulgakov, M.R. Predtechensky, Institute of Thermophysics SB RAS, prosp. Lavrentyev 1, 630090 Novosibirsk, Russia
Photoluminescent (PL) properties of the nanostructured silicon films produced by pulsed laser ablation of silicon target in an ambient gas have been studied. Three PL bands in visible wavelength range ("blue", "yellow" and "red") are observed. The intensity of each band depends variously on deposition conditions (parameters of the laser radiation, pressure and type of ambient gas). The mass composition and energies of the particles generated in the laser plume under actual deposition conditions have been investigated using time-of-flight mass-spectrometry in combination with molecular beam technique. It is shown that the quantity of matter transported by the clusters to substrate sharply increases with increasing of the pressure from 1 to 1000 mTorr. It is determined that increase of PL intensity of the "yellow" and "red" bands take place for deposition conditions corresponding to efficient cluster formation. Investigation of the film microstructure by the TEM has shown that the films with PL in the "yellow" and "red" bands have nanostructure with scale of about 10 nm. It is shown experimentally that the clusters produced in the plume during laser ablation play an important role in formation of the nanostructured luminescent silicon films.
- B-II/P15** PHOTOLUMINESCENCE AND PARAMAGNETIC DEFECTS IN SILICON-IMPLANTED SILICON DIOXIDE LAYERS, V.Ya. Bratus', M.Ya. Valakh, A.A. Konchits, V.A. Yuhimchuk, Institute of Semiconductor Physics, NASU, 45 pr. Nauky, 252028 Kiev, Ukraine; P.L.F. Hemment, Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey, UK and T. Komoda, MEW Ltd, Osaka, Japan
Thermally grown SiO₂ on Si substrate implanted by Si⁺ ions with a dose of 6.10¹⁶ cm⁻² were studied by photoluminescence (PL), electron paramagnetic resonance (EPR) and low-frequency Raman scattering. The implanted samples were thermally annealed in nitrogen ambient at temperatures ranging from 300°C to 1200°C. The wide structureless EPR line at a zero crossing g=2.0005 dramatically changed its shape even after the first anneal at 300°C. The E'γ center, EP2 center, E'δ-like and non-bridging oxygen hole center were identified. The PL intensity in the 620 nm range was found to correlate with total number of paramagnetic defects. Low-temperature hydrogen-content plasma treatment of the samples by first annealed up to 600°C led to disappearance both EPR and 620 nm PL band. No detectable EPR spectra were recorded from the samples annealed at T>1100°C which revealed strong red PL band at λ=740 nm. A further evidence that this PL band can be attributed to formation of Si nanocrystallites in SiO₂ matrix was provided by low-frequency Raman scattering measurements where a weak line at 60 cm⁻¹ was observed. This "breathing" mode corresponds to 4 nm average diameter of Si nanocrystallites.
- Rare Earth Doping**
- B-II/P16** ERBIUM IN SILICON-GERMANIUM QUANTUM WELLS, M.Q. Huda, A. Scholes, A. Naveed, J. Hartung, J.H. Evans-Freeman, A.R. Peaker, Centre for Electronic Materials, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK; D.C. Houghton, SiGe Microsystems Inc., Ottawa, Canada, K1A 0R6; J.M. Fernandez, B.A. Joyce, Imperial College, London SW7 2BZ, UK; C. Jeaynes, W.P. Gillin, University of Surrey, Guildford, Surrey, UK
Erbium has been implanted into Si/Si_{1-x}Ge_x/Si multiple quantum wells (0.01 < x < 0.12) with a sequence of energies in the range 0.3 to 1 MeV so that [Er] = 10¹⁸ cm⁻³ throughout the active region. The necessary erbium dose is insufficient to produce complete amorphisation of the SiGe structures so an amorphising implant of silicon has also been used. Solid phase regrowth has been effected at low temperature (~650°C). In all cases the SiGe layers were below the critical thickness (Paine criteria). The luminescent, electrical and structural behaviour has been compared with similar implants into Czochralski silicon of similar oxygen content. Chemical and structural studies (SIMS, TEM and double crystal X-ray) show perfect regrowth with no measurable segregation of the germanium or erbium and no formation of dislocations. However, although the erbium luminescence from the layers is extremely efficient (we estimate 12% internal quantum efficiency at 77K) a broad luminescent band ascribed to germanium complexes is evident. This is discussed in relation to the crystal field splitting and the thermal quenching of the luminescence.

- B-II/P17** OPTICAL PROPERTIES OF EUROPIUM DOPED SILICON NANOCRYSTALS, J. Qi, T. Matsumoto, M. Tanaka and Y. Masumoto, Single Quantum Dot Project, ERATO, Japan, Science and Technology Corporation, Tokodai 5-9-9, Tsukuba, Ibaraki 3002635, Japan

Silicon nanostructure attracts a special interest from the viewpoint of the intense visible emission. As the size of Si nanocrystal (nc-Si) decreased, its band gap shifts to the higher energy due to the quantum size effect. This fact suggests that nc-Si may be used as an effective host material for the optical active ions (e.g. rare earth). In this work, we have prepared Eu^{2+} doped nc-Si samples by radio frequency sputtering method and the post-annealing process, and investigated their optical properties. We found that the photoluminescence spectrum of Eu^{2+} in nc-Si: Eu^{2+} shows a strong emission band (peak at 2.53 eV, FWHM \sim 420 meV) different from that Eu^{2+} in SiO_2 (peak at 3.05 eV, FWHM \sim 98 meV). These observations can be explained by the host dependent effect of the Eu^{2+} emission.

- B-II/P18** OPTICAL PROPERTIES OF NEODYMIUM INCORPORATED IN POROUS SILICON, R. M'ghaïeth, J.C. Vial, M. Haouari, H. Maaref, Faculté des Sciences de Monastir, Route de l'Environnement, 5000 Monastir, Tunisia

The incorporation method of rare earth (RE) doped semiconductors is an important factor for the luminescence. For crystalline semiconductors, the implantation, ion-assisted deposition or the thermal diffusion are well used techniques. Recently, because of the discovery of porous silicon luminescence, some groups attempted the introducing of RE ions in porous silicon by electrochemical method and adapted thermal treatments activating the luminescence properties. The pumping method was used to introduce NdCl_3 solution in silicon pores and then thermal treatment was necessary to obtain an efficient luminescence. Prior to annealing, the luminescence could be observed from the as-prepared samples but vanishes when the samples were kept in room atmosphere. The annealing, needed to optically activate RE ions was performed in a conventional furnace tube at temperatures ranging from 700 to 1000°C for 60s under flowing humid hydrogen atmosphere.

This paper reports the results of Photoluminescence and Photoluminescence Excitation studies on Neodymium doped porous silicon. The main result is that the dispersion of RE ions is an active parameter in the establishment of the luminescence and no energy transfer was observed.

- B-II/P19** COMPARISON STUDY OF DONOR FORMATION IN HOLMIUM, DYSPROSIUM, AND ERBIUM-IMPLANTED SILICON, V.V. Emtsev, V.V. Emtsev, D.S. Poloskin, E.I. Shek, and N.A. Sobolev, Ioffe Physicotechnical Institute, 194021 St.Petersburg, Russia

The purpose of this work is to compare the formation of donors in Si doped with Ho, Dy, and Er by means of ion implantation (1 MeV).

After the annealing at 700°C of Si:Ho, Si:Dy, and Si:Er, the formation of shallow donors with ionization energies spreading from \approx 30 meV to \approx 40 meV are observed. They are attributed to oxygen-related thermal donors. In both Si:Ho and Si:Dy, other donor states with a single ionization energy of \approx 60 meV also make their appearance. They differ from those at $\approx E_C - 70$ meV observed in Si:Er. These centers are claimed to be associated with rare-earth dopants, most likely in complex form. After the annealing at 900°C, the concentrations of oxygen-related shallow donors and centers at $\approx E_C - 60$ meV (Si:Ho and Si:Dy) or 70 meV (Si:Er) are strongly reduced. New donor states slightly below $E_C - 0.1$ eV develop in considerable concentrations.

- B-II/P20** LOCAL ENVIRONMENT SYMMETRY OF ERBIUM IMPURITY ATOMS IN AMORPHOUS HYDROGENATED SILICON, V.Kh. Kudoyarova, A.N. Kuznetsov, E.I. Terukov, A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St.Petersburg, Russia, V.F. Masterov, F.S. Nasredinov, P.P. Seregin, St.Petersburg State Technical University, 195251 St.Petersburg, Russia

Recently we have observed photoluminescence (PL) and electroluminescence (EL) in erbium doped amorphous hydrogenated silicon (a-Si:H:Er). It was shown that the PL intensity at room temperature is two orders of magnitude higher than in crystalline silicon c-Si:Er. By analogy with c-Si:Er, we have postulated that emitting center in a-Si:H:Er are [Er-O] clusters although they do not provide direct evidence to support this. In the present study a-Si:H:Er samples were analyzed by emission Mossbauer spectroscopy utilizing the ^{169}Er (^{169}Tm) isotope to identify the local environment symmetry of the erbium ions in a-Si:H.

Films of a-Si:H:Er were obtained by magnetron sputtering of a metallic erbium target in silane-argon atmosphere. The oxygen and hydrogen concentrations were determined by secondary ion mass spectrometry. In all the films studied the oxygen concentration was constant at $\approx 10^{21} \text{ cm}^{-3}$. The erbium concentration (N_{Er}) and its distribution profile were determined by Rutherford backscattering. The N_{Er} in these films varied between 10^{19} and 10^{21} cm^{-3} . The PL spectra were recorded at room temperature, the PL being excited by the 488 nm argon laser line.

In particular the Mossbauer spectra of a-Si:H:Er samples correspond to two states of Er impurity in the structural network of a-Si:H (1 and 11), where spectrum 1 corresponds to Er centers with reduced local environment symmetry and spectrum 11 corresponds to Er centers in an almost regular cubic environment. Since the relative intensity of spectrum 1 increases with increasing PL intensity, these erbium states are responsible for the PL of a-Si:H:Er. The parameters of spectrum 1 are similar to those of the emission Mossbauer spectrum of $^{169}\text{Er}_2\text{O}_3$ and it may be concluded that the PL centers are [Er-O] clusters, where the local symmetry of the Er^{3+} ions in these clusters is similar to that of Er_2O_3 .

- B-II/P21** ROOM-TEMPERATURE PHOTOLUMINESCENCE OF AMORPHOUS HYDROGENATED SILICON CARBIDE DOPED WITH ERBIUM, V.Kh. Kudoyarova, E.I. Terukov, A.N. Kuznetsov, Ioffe Physico-Technical Institute, 194021 St-Petersburg, Russia; W. Fhus, Hahn-Meitner Institut, Rudower Chaussee 5, 12489 Berlin, Germany; G. Weiser and H. Kuehne, Fachbereich Physik Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

Recently the luminescent properties (PL and EL) of erbium-doped crystalline silicon (c-Si:Er) have attracted much attention. However, the PL of c-Si:Er is strongly quenched with increasing temperature. It has been shown that the intensity of the Er emission strongly depends on the band gap energy of the host semiconductor, mainly for the room temperature emission.

In this paper, the results obtained by us on erbium-doped amorphous hydrogenated silicon (a-Si:H:Er) are extended to erbium-doped amorphous hydrogenated silicon carbide (a-Si_{1-x}C_x:H:Er) to increase the band gap energy limit. It is shown that a-Si_{1-x}C_x:H:Er exhibit strong room-temperature PL at 1.54 μm , which is assigned to the internal 4f-shell transition in Er ions.

Films of a-Si_{1-x}C_x:H:Er have been prepared by cosputtering of graphite and Er targets applying the magnetron-assisted silane-decomposition (MASD) technique. The composition of films (x) and the presence of Er in the films have been monitored by RBS, (x) was varied in the range 0 - 0.29. The concentration of incorporated Er-ions was $6 \times 10^{19} \text{ cm}^{-3}$. The optical band gap was determined by CPM varied from 1.59 (x = 0) to 1.82 eV (x = 0.29).

It was shown that the onset of temperature quenching of PL in the case of a-Si_{1-x}C_x:H:Er is observed at higher temperatures than for a-Si:H:Er and c-Si:Er and the quenching less pronounced. The weak temperature dependence of PL in a-Si_{1-x}C_x:H:Er is discussed in the terms of the model previously proposed by us for a-Si:H:Er. In this model the mechanism of electronic excitation of Er ions is based on defect-related Auger excitation.

- B-II/P22** PHOTOLUMINESCENCE FROM POROUS SILICON ELECTROCHEMICALLY DOPED WITH ERBIUM, L. Dolgyi, S. Volchek, N. Kazuchits, V. Yakovtseva, V. Bondarenko, Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus; and L. Tsybeskov, H. Lopez, G. Grom and Ph. Fauchet, University of Rochester, Rochester NY, USA

Porous silicon (PS) doped by Er (PS:Er) is shown to be promising for optoelectronic application. In this work we present a study of photoluminescence from PS:Er prepared by combination of electrochemical anodic-cathodic treatments followed by high temperature annealing. PS layers with dendritic and sponge structure of 0.5-10 μm thick and of 10-70% porosity were formed by anodization in HF electrolytes. Incorporation of Er was performed via the cathodic polarization of PS in electrochemical bath containing Er salt and organic solvent. Electrochemical processing of PS samples was followed by high temperature treatment in the oxidizing atmosphere to provide partial or total oxidation of PS:Er layer. The emission and excitation spectra were studied. After thermal treatment, a strong Er-related photoluminescence at 1.54 μm was observed. Both PS thickness and porosity as well as the conditions of PS processing have a profound impact on the luminescence intensity. The mechanism of Er-related luminescence and possible applications of the partially and fully oxidized PS:Er structures for LEDs and for integrated waveguides are discussed.

- B-II/P23** LUMINESCENCE FROM POROUS SILICON DOPED WITH ERBIUM-ITTEBIUM COMPLEXES, V. Filippov, V. Kuznetsova, V. Homenko, P. Pershukovich, Belarussian Academy of Sciences, F.Skorina 70, 220072 Minsk, Belarus; V. Yakovtseva, Belarussian State University of Informatics and Radioelectronics, Brovka 6, 220027 Minsk, Belarus, and M. Balucani, V. Bondarenko, G. Lamedica and A. Ferrari, INFN UNIT E6 Università 'La Sapienza' di Roma, Via Eudossiana 18, 00184 Roma, Italy
Features of photoluminescence from porous silicon (PS) doped with erbium-ytterbium complexes have been demonstrated. Erbium-ytterbium complexes were introduced into PS films by long standing in colloidal solution of $\text{GdOCl}:\text{Er}, \text{Yb}$ followed by high temperature treatment at 1100°C . Strong room-temperature photoluminescence from PS doped with Er-Yb complexes was disclosed at 1.0 and 1.53 μm . On excitation with radiation of wavelength matched the PS absorption band, IR emission from $\text{Er}^{3+}+\text{Yb}^{3+}$ containing films increased several times in intensity. We attributed the phenomenon to the transfer of excitation energy between PS, Er^{3+} and Yb^{3+} ions as well as to the effect of cross-relaxational multiplication of IR excitations within the Er^{3+} ions. The role of defects of an oxide envelope of the silicon nanocrystallites in excitation process of PS doped with erbium-ytterbium complex is discussed.
- B-II/P24** ON THE ORIGIN OF 1.5 μm LUMINESCENCE IN POROUS SILICON COATED WITH SOL-GEL DERIVED ERBIUM DOPED Fe_2O_3 FILMS, N.V. Gaponenko, A.V. Mydryi, O.V. Sergeev, V.E. Borisenko, Belarusian State University of Informatics and Radioelectronics, P.Browki str.6, 220027 Minsk, Belarus; M. Stepihova, L. Palmetshofer, W. Jantsch, Institut für Halbleiterphysik, Johannes-Kepler-Universität Linz, 4040 Linz-Auhof, Austria; J.C. Pivin, Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, Bâtiment 108, 91405 Orsay Campus, France; A.S. Baran, A.I. Rat'ko, Institute of General and Inorganic Chemistry, Surganova str. 9, 220027 Minsk, Belarus
Sol-gel derived Fe_2O_3 films contained about 10 wt% of Er_2O_3 were deposited on porous silicon by dipping or spin-on technique followed by thermal processing at 1073 K for 15 min. The samples were characterised by the means of PL, SEM and RBS analyses. They exhibit strong room-temperature luminescence at 1.5 μm related to erbium in sol-gel derived host. The luminescence intensity increased by a factor of 1000 when the samples are cooled from 300 to 4.2 K. After complete etching of the erbium doped film and partial etching of the porous silicon the erbium-related luminescence disappears. In so doing the luminescence at 1.5 μm originating from optically active dislocations ("D-lines") in porous silicon is detected. The influence of the conditions of synthesis on luminescence at 1.5 μm is discussed.
- B-II/P25** ROOM TEMPERATURE GREEN PHOTOLUMINESCENCE FROM Er IONS IN AMORPHOUS SiN FILMS, A.R. Zanatta, L.A.O. Nunes, M.J.V. Bell, Instituto de Física de Sao Carlos, Universidade de Sao Paulo, P.O. Box 369, 13560-970 Sao Carlos, S.P. Brazil
Green light emission at room temperature was achieved from non-hydrogenated amorphous silicon-nitrogen (a-SiN) thin films. The films were deposited by cosputtering a Si target covered with small metallic Er platelets in an Ar^+N_2 atmosphere. According to the adopted deposition conditions the nitrogen concentration [N] reached ~40 at.% rendering an optical gap of approximately 3.5 eV. The Er concentration [Er] was estimated to be ~10 at.% in the present films. Photoluminescence spectroscopy were performed in the 300-77 K temperature range on as-deposited films with the help of different excitation wavelengths of an Ar^+ laser. The large optical band-gap of these films, associated to the high Er concentration, allows the direct excitation of Er^{3+} ions being more efficient at lower temperatures and when exciting with 488 nm photons (in resonance with the $\text{Er}^{3+} F_{7/2}$ energy level). In addition to light emission at ~520 and ~545 nm, transitions in the infrared energy region (at ~980 and ~1540 nm) could be easily verified.
- B-II/P26** 1.54 μm EMITTING ERBIUM-DOPED a-Si:H FILMS FABRICATED BY STANDARD PECVD USING METALLOORGANIC $\text{Er}(\text{HFA})_3 \cdot \text{DME}$, N.A. Feoktistov, V.G. Golubev, A.V. Medvedev, Yu.A. Nikulin, A.B. Pevtsov, Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia and N.I. Gorshkov, D.N. Suglovov, Chlopin Radium Institute, 194021, St. Petersburg, Russia
Hydrogenated amorphous Si thin films prepared by standard PECVD at low substrate temperature (200 C) were doped with Er during the deposition by making use of a new fluorine containing metalloorganic (MO) compound $\text{Er}(\text{HFA})_3 \cdot \text{DME}$ ($\text{HFA}=\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$, $\text{DME}=\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$). The MO powder was placed into a stainless steel container close to a glow discharge volume. The sublimation rate of the powder was operated by heating within the range of (20-200) C. The 300 nm thick films were deposited on glass, fused quartz and Si wafers. Photoluminescence (PL) spectra of a-Si(Er):H films were studied within the range of 0.6-1.7 μm at both 77 K and 295 K. A strong room-temperature PL at 1.54 μm was observed. A photoconductivity (ratio of $\rho_{\text{photo}}/\rho_{\text{dark}}=10^3$) was detected too. The impurity concentrations of erbium and fluorine measured by SIMS were around 10^{19}cm^{-3} and $3 \times 10^{20}\text{cm}^{-3}$ correspondingly. PL measurements at 77 K have revealed two strong lines (centered at 0.96 μm and 0.64 μm) to appear in addition to Er emission. The 0.96 μm line resulted from "tail-tail" transitions in a-Si:H and the 0.64 μm line is connected with carbon incorporation in the films. Effect of the deposition parameters, temperature of measurements and laser excitation power on erbium PL will be discussed.
The work was supported by the Russian Foundation of Basic Research.
- B-II/P27** LOW-TEMPERATURE ANNEALING EFFECT ON 1.54 μm EMISSION OF Er-DOPED a-Si:H, A.A. Andreev, V.G. Golubev, I.V. Korkin, A.V. Medvedev, V.B. Voronkov, Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia
Doped with Er hydrogenated amorphous Si films have been prepared by both DC magnetron sputtering of Er-Si composite target (type I) in the gas mixture of Ar with H_2 diluted SiH_4 and standard PECVD (type II) using metalloorganic $\text{Er}(\text{HFA})\text{DME}$ ($\text{HFA}=\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3$, $\text{DME}=\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$). The deposition temperature was 200 C. The Er concentration measured by SIMS was varied from 10^{19}cm^{-3} to $6 \times 10^{20}\text{cm}^{-3}$ depending on the deposition technique used. As-grown films demonstrated a weak 1.54 μm photoluminescence (PL) intensity of Er^{3+} ion under Ar (488 nm) line excitation. Then the thermal annealing within the range of 200-700 C for 15 min in N_2 atmosphere were carried out. The 1.54 μm PL intensity at 77 K appears to be extremely enhanced by a factor of 50 for the both film types at the annealing temperature as low as 300 C. The temperature quenching of PL measured in linear regime of pumping was no more than 4-5 times from 77 K to 300 K. No Er-related PL was observed after the annealing at $T>500$ C. The effect of cumulative annealing on 1.54 μm PL intensity was investigated too. We discuss the annealing process in the frame of a model of a partial structural rearrangement of a-Si:H amorphous network and simultaneous optical activation of erbium centers in the process of hydrogen release from weak Si-H-Si bonds in the 300 - 400 C interval.
The work was supported by the Russian Foundation of Basic Research.

Porous Silicon

- B-II/P28** OPTICAL WAVEGUIDES IN POROUS SILICON PRE-PATTERNED BY LOCALISED NITROGEN IMPLANTATION, H. Arrand, T.M. Benson, P. Sewell, University of Nottingham, Nottingham, UK; A. Loni, Defence Evaluation and Research Agency, Malvern, UK

FIPOS technology forms islands of silicon isolated from a silicon substrate by (oxidised) porous silicon. The larger refractive index of the silicon islands suggests their use as optical waveguides. Sets of these silicon islands were formed by a two-stage N⁺ implantation through a patterned photoresist mask. Following mask removal, the wafers were anodised and annealed. The anticipated waveguiding in the silicon islands was observed experimentally at 1.3 μm , although it proved difficult to excite.

However, the dominating waveguiding was, surprisingly, located in the porous silicon *between* silicon islands, close to the sample surface. These waveguides also operated at 1.15 μm in the as-prepared state and at 0.633 μm following oxidation. A second guided mode adjacent to the porous silicon-silicon substrate interface was also seen.

These experimental results are explained by a simple dynamic model for the anodization of porous silicon, based on an equivalent network model of the current flow and assuming a 'silicon', 'anodizing' or 'anodized' (porous) state. The model uses a look up table to determine the porosity and anodization rate as a function of current. The waveguide regions observed experimentally are shown to correspond to areas of reduced porosity (increased refractive index).

- B-II/P29** INTEGRATED WAVEGUIDES BASED ON OXIDIZED POROUS SILICON:FORMATION AND OPTICAL PROPERTIES, M. Balucani, V. Bondarenko, L. Franchina, G. Lamedica and A. Ferrari, INFN Unit E6, University 'La Sapienza', Rome, Italy; and N. Vorozov, V. Yakovtseva, Belarussian State University of Informatics and Radioelectronics, Brovka 6, 220027 Minsk, Belarus; and V. Filippov, A. Tomov, Institute of Physics, Belarussian Academy of Sciences, F. Skorina 70, 220072 Minsk, Belarus

Production of integrated optoelectronic systems required low-cost technologies of optical interconnections. In the present paper we demonstrate the specific features of the original technology of integrated waveguides based on oxidized porous silicon (OPS). This technology is compatible with the conventional silicon technology of microelectronic devices manufacturing, resulting in the advisability of OPS-based waveguides use in integrated optoelectronics. The method shows considerable promise as a mean for optical interconnections within one silicon chip to produce integrated optoelectronic circuit on-chip. The latest results are reported. Refractive indexes in the waveguiding channel as well as at the waveguide-substrate interface are presented. Integration of waveguide and amorphous silicon photodetector on-chip is demonstrated.

- B-II/P30** THE ORIGIN OF LIQUID-PHASE ELECTROLUMINESCENCE FROM POROUS SILICON, J.D. Moreno, R. Guerrero-Lemus, R.J. Martin-Palma, J.M. Martinez-Duart, M.L. Marcos and J. Gonzalez-Velasco, Dpto de Fisica Aplicada and Dpto. de Quimica C-IX, Univ. Autonoma de Madrid, 28049 Madrid, Spain

Electroluminescence (EL) of porous silicon (PS) immersed in an electrolyte has been previously attributed to radiative recombination of holes from the bulk silicon and electrons injected by species absorbed at the surface. We propose in this work the HO₂ radicals produced by the water oxidation as the species responsible for the electronic injection in the EL emission mechanism, discarding the oxidation of Si-H bond as possible source of these electrons.

This assumption is confirmed by the study of the porous silicon surface by Fourier transform infrared spectroscopy, according to which the concentration of Si-H_x bonds remains constant during the time interval in which the electroluminescence is recorded.

- B-II/P31** INTEGRATION OF A POROUS SILICON LIGHT EMITTING DIODE AND A WAVEGUIDE BASED ON A MULTILAYER ALUMINA STRUCTURE, S. Lazarouk, P. Jaguiro, Belarussian State University Informatics and Radioelectronics, P.Brovki 6, 220027, Minsk, Belarus

Recently we have reported on an aluminum - porous silicon light emitting diode (LED) connected with a photodetector by an alumina waveguide. In this paper the waveguide design has been improved by application of a multilayer alumina structure with different concentration of TiO₂ doping. The alumina waveguide structure has been fabricated by magnetron sputter deposition of an aluminum film with subsequent anodic oxidation. The aluminum film has been deposited by magnetron sputtering from three targets. The first and the third targets were pure aluminum. The second one was aluminum with 2 weight percentages of Ti. After anodic oxidation the multilayer alumina structure has been formed with different concentration of TiO₂ doping. The refractive index of the second core alumina layer was higher in comparison with the first and the third layers. Integration of porous silicon LED and alumina waveguide based on the multilayer structure has showed increasing of output signal in comparison with before reported dates.

- B-II/P32** AVALANCHE LED ON MONOCRYSTAL AND POROUS SILICON, P. Jaguiro, JV'Belaya Vezha', Chorny Str. 9A, 220012 Minsk, Belarus and S. Lazarouk, BSUIR, Brovki Str. 6, 220600 Minsk, Belarus

Rather efficient visible light emissive diodes can be realized even on monocrystal silicon by using the special topology. For example, there are known LED-s on monocrystal Si - with silver islands /1/, silver dust or Al film (after special anodization process) /2/. Visible light in such devices is emitted due to hot electrons and holes produced by avalanche. High emission efficiency in such devices is achieved by forming a lot of sub-micro and nano-junctions, corresponded changing the avalanche conditions, great heating of electron gas and blue shift of the gas emissive spectrum /2/. When we use porous Si, the same mechanism takes place, but nano-junctions are formed due to Si morphology, but not due to cover metal one. By changing porous Si morphology it is possible to control the number and size of nano-junctions to improve the light emission efficiency /3/. But the main difference is not in number or size of the junctions; it is in changing the electro-physical and optical parameters of porous Si. Numerical calculations by method described in /2/ were carried out to find trends of spectrum and efficiency via porous Si parameters. In addition, to correct external emission efficiency the light transmission coefficient from porous Si is calculated.

1. Dobson P. ..., US patent N 5567954 (1996) 2. Jaguiro P. ..., "Reasons of high efficiency visual EL in monocrystal silicon", ECS Meeting 192nd - Aug 31 - Sept 5, 1997 - Paris, France 3. Lazarouk S. ..., Applied Physics Letters, v.68 N 15 pp.2108-2110 (1996)

- B-II/P33** NEW PEAKS IN INFRARED ELECTROLUMINESCENCE OF REVERSE BIASED POROUS SILICON LIGHT EMITTING DIODES, S. Lazarouk, P. Jaguiro, V. Borisenko, Belarussian State University Informatics and Radioelectronics, P.Brovki 6, 220027 Minsk, Belarus

Light emission from reverse biased porous silicon light emitting diodes covers both visible and infrared ranges. The infrared part has been observed to be composed of different peaks. Besides the intrinsic radiation of silicon at 1.1 μm , we have resolved other peaks which are around 1.3 - 1.5 μm . It is important to mention that the similar peaks have been also detected in the porous silicon structures which does not emit light in the visible range. Meantime it is known that dislocations in silicon can be electrically and optically active due to related local energy levels introduced in the forbidden gap. Also it is known that porous silicon is the dislocation-rich material. Thus we suppose that the peaks of electroluminescence around 1.3 - 1.5 μm relate to the dislocations in porous silicon or in the monocrystalline region just at their interface. The application of this effect for the modification of porous silicon light emitting diodes has been discussed.

- B-II/P34** DETERMINATION OF LOCALIZED STATES IN POROUS SILICON, T. Matsumoto, J. Qi, Y. Masumoto, Single Quantum Dot Project, ERATO, JST 5-9-9 Tokodai, Tsukuba 300.26, Japan and N. Koshida, Tokyo University of Agriculture and Technology, Tokyo 184, Japan
A space-charge-limited current (SCLC) flow as a function of applied bias potential and specimen thickness were studied for porous silicon films prepared by electrochemical anodization. From the analysis of the current-voltage and the current-thickness characteristics in the SCLC regime, the localized state distribution near the Fermi level in porous Si were determined by step-by-step methods [1]. We will show that the density of states determined by the SCLC measurements well explain the current-voltage characteristics of other samples.
[1] K. D. Mackenzie et al., Philos. Mag. B 46 (1982) 377.
- B-II/P35** POROUS SILICON: PREPARATION AND CHARACTERIZATION FOR ELECTROLUMINESCENT APPLICATIONS, I. Kleps, A. Angelescu, IMT, PO Box 38-160, 72996 Bucharest, Romania
Porous silicon preparation, morphology, chemical composition and electrical characterization are evaluated in connection with the possibility to use this material for electroluminescent applications.
PS layers were prepared by an electrochemical process on (100) p-Si wafers with resistivity of 10-30 Ωcm , followed by different stabilization processes. Porous silicon layers of medium and high porosity (60 %, respectively 80 %) and 3-5 μm thick were prepared and characterized. The top electrodes were realized by: 1) vacuum depositing (with two different speed deposition) and heat treatment process for Al and In-Au; 2) electrochemical process for Au.
The PS layers morphology was investigated by SFM, their composition by SIMS, and the electrical properties and the influence of different metallic contacts are studied from I-V and C-V measurements on MIS devices.
All the contacts show a rectifying behavior. The best results were obtained on 80 % porosity PS, anodically oxidised and with ITO as top metal. The contact resistance is low, the ideality factor, n , at low injection levels presents values between 2,5-3 and the value for series resistance is $< 500\Omega$.
- B-II/P36** POROUS SILICON LAYERS APPLIED TO SILICON SOLAR CELLS AND LIGHT EMITTING DIODES, D. Dimova-Malinovska, Central Laboratory for Solar Energy and New Energy Sources, Bulg. Acad. Sci., Tzarigradsko chaussee 72, 1784 Sofia, Bulgaria
The application of porous silicon in crystalline silicon solar cells and in light emitting (LE) heterostructures is reported. Porous silicon was prepared by the method of stain-etching of the Al covered surface of a c-Si wafers in etching solution $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=1:3:5$. Different c-Si substrates were used - p-type and n^+-p junction. In the case of LE structures a ZnO highly conductive thin film was used as a front transparent contact. The transport properties in the different structures are studied. A model based on multi-step tunneling of minority carriers through a narrow energy barrier is suggested for describing the properties of PS heterostructures. Applying porous silicon layer between the fingers of the frontal electrode in crystalline silicon solar cells leads to an increase of short circuit current by about 40%, of efficiency by about 30% and of the spectral response in comparison with the reference cells.
- B-II/P37** THE DECAY KINETICS OF POR-Si ELECTROLUMINESCENCE AND RELAXATION PROCESSES AT POR-Si/Si HETEROSTRUCTURES, P.V. Galiy, T.I. Lesiv, L.S. Monastyrskii, T.M. Nenchuk, I.B. Olenych, O.Ye. Fl'unt, Physical Department, Lviv State University, 50 Dragomanov str., 290005 Lviv, Ukraine
The electroluminescence (EL) of por-Si/Si heterostructure in contact with electrolyte under excitation by square pulses of current has been studied. The EL spectrum revealed wide luminescence band in 500-900 nm range. The EL relaxation processes were studied taking into account the spectral decay of intensity at the intervals between the exciting pulses. The existence of various, according to decay kinetics, luminescence centres at por-Si: "short wave" with rapid and "long wave" with slow decay has been established.
The complex of complementary methods: Auger electron spectroscopy (AES), thermally stimulated exoelectron emission (TSEE) and depolarization current (TSDC) and low frequency dielectric spectroscopy (LFDS) have been applied for investigation of the EL nature and luminescence centres. The availability of dielectric coatings and charge trapping centres were established by TSEE and TSDC methods and AES analyses revealed their composition ($\text{Si}_x\text{O}_y\text{C}_{1-x-y}$) and effective thickness (1.7-4.1 nm). The peculiarities of charge carriers transport and relaxation by localized states were studied by LFDS. Dielectric coatings' high thickness and effective area might play a significant role in EL of por-Si/Si and its relaxation kinetics.
- B-II/P38** ELECTROLUMINESCENT p-n STRUCTURES WITH POROUS SILICON, T. Gorbach, S. Svechnikov, P. Smertenko, D. Voronkov, ISP NASU, Nauki avenue 45, 252028 Kyiv, Ukraine; N. Vorozov, L. Dolgyi, N. Kazuchits, BSUIR, P.Brovki Street 6, 220027 Minsk, Belarus and R. Chiah, J. Morgel, IMMS PAS, Reymonta Street 25, 30059 Krakow, Poland
Two types of the visible light emitting p-n structures on porous Si (PS) have been investigated. The first type is n^+ -polySi/p-PS/p-Si/Al and the second one is ITO/p-PS/p-Si/Al. Analyses of current-voltage characteristics have been carried out using $\alpha = d(\lg I)/d(\lg V)$ diagnostic peculiarities of charge flow and carriers injection. The first structure demonstrates visible electroluminescence (EL) from discrete points in both bias directions. The forward $\alpha(V)$ dependence increases at low biases, has a maximum in the range less than 5 V, then decreases to $\alpha=1$ and increases once more. The very low EL efficiency in these structures are mainly due to not enough minority carriers injection. The second type of structure shows the qualitatively analogous behavior of forward I-V and $\alpha(V)$ characteristics but with some important features: (i) α_{max} is at lower biases; (ii) the $I \sim V^2$ dependence which corresponds to monomolecular recombination regime. The reverse I-V characteristic has $\alpha=3$ and $\alpha=4$. These improve that the heterojunction I-V characteristics take place. The TEM and SEM cross sections image of structures have been presented and analyzed. The main directions for the enhance of the EL efficiency have been discussed.
- B-II/P39** PECULIARITIES OF CHARGE INJECTION INTO POROUS SILICON IN TEMPERATURE RANGE FROM 77 K TO 400 K, G.O. Sukach, P.Ph. Oleksenko, P.S. Smertenko, A.M. Evstigneev, A.B. Bogoslovskaya, V.Yu. Goroneskul, ISP NASU, prospekt Nauki 45, 252028 Kyiv, Ukraine
The Au and Al contacts have been used to investigate the peculiarities of charge injection into porous silicon structures fabricated by electrochemical technique on 20 Ωcm p-type silicon.
The current-voltage characteristics (CVC) at temperatures (T) 77 K, 293 K and 373 K were analysed by differential slope in log-log scale. This treatment gives the values $\alpha = d \lg I / d \lg V$ and $\gamma = d \lg \alpha / d \lg V$ which identify the regions $I \sim V^\alpha$ and $I \sim \exp V^\gamma$.
At room temperature the forward CVC have the exponential region with ideality coefficient (β) of about 16. Then the regions $I \sim V^2$ and $I \sim V^{3/2}$ follow for Au and Al contacts and correspond the monomolecular and bimolecular recombination, respectively. The temperature dependence of βkT (k - the Boltzmann constant) for Au-porSi-Si-Al structure was constant in all temperature range investigated. This indicate tunneling mechanism of charge flow.
The effective life time of minority charge carriers (τ) decreased when the current increased. The same τ behaviour was for temperature increasing. This point out the nonexponential character of τ kinetics therefore kinetics is stipulated for the recombination of electrons localized in potential wells of various depth with free or localized (what more probably) holes.
As the conclusion, the main charge flow mechanism is the tunneling processes through thin dielectric in our porSi structures and the current is restricted by generation in space charge region and recombination through surface states at Si-SiO₂ boundary.

B-II/P40 EFFECT OF FREQUENCY AND MAGNETIC FIELD ON CAPACITANCE OF STRUCTURES BASED ON POROUS SILICON, N.S. Averkiev, A.A. Lebedev, A.D. Remenyuk, N.N. Smirnova, Power Devices Laboratory, Ioffe Physical-Technical Institute, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia

The discovery of bright room-temperature luminescence from porous Si has evoked a lot of scientific interest to porous semiconductor properties mostly in optical direction. The electrical properties are less investigated. The presented paper partly fills the gap. The screening efficiency of extrinsic electric field by charge carriers depends on the dimensionality of space which limits the particle movement. So the type of electrical capacitance frequency dependence of nano-dimensional structures may depend on their dimensionality. As a result the dispersion of sample electric capacitance may take place. The effects of frequency and of magnetic field on capacitance were revealed and investigated in this report on the structures using the porous Si and porous 6H-SiC, which can be considered as an continuum including nanodimensional conducting crystallites. The observed frequency dependence of capacitance was found characteristic of presence of two-dimensional conducting planes with characteristic thickness $d=1\mu$. We have also revealed the effect of magnetic field on capacitance at $H \leq 13$ kG in frequency range from 0.1 Mgz to 1 Mgz.

B-II/P41 ELECTRON TRANSPORT IN POROUS AMORPHOUS SILICON, A.I. Yakimov, N.P. Stepina, A.V. Dvurechenskii, Institute of Semiconductor Physics, Novosibirsk, Russia

Investigation of electrical properties of porous silicon is important for the electroluminescence silicon devices. However large depletion range in thin wires of crystalline silicon makes a big problem for studying of the electron transport in crystalline porous silicon. These difficulties are excepted in amorphous porous silicon (a-PS), so its electrical characteristics allows to obtain an information about peculiarities of structure of porous silicon. We report measurements of dc and ac conduction in steady-state regime, kinetics of conductivity relaxation, current noise in a-PS with porosity 15-45%. Experimental results demonstrate that charge transport in a-PS is associated with fractal structure of internal silicon surface. These results include the temperature dependence of dc conductivity (the low $T^{3/7}$), non-exponential slow conductivity relaxation of the form $\sigma(T) \sim \exp[-(t/\tau)^\beta]$ with $\beta \sim 0.56$, spectral density of excess current fluctuations, depends on frequency as $1/f^{1.26}$. Various fractal dimensions (spectral dimension, random walk dimension and Hausdorff geometrical dimension) were determined from the analysis of experimental data. The temperature - induced transition from 3D to 1D variable range hopping conduction in the network of parallel quantum wires have been observed in a-PS. Superlocalization exponent and diameter of silicon wires were deduced from the analysis of dc and ac conductivity.

This work was supported by the Russian Federal Program "Surface Atomic Structures" through the Grant 97-3.21.

B-II/P42 ABSENCE OF CARRIER HOPPING IN POROUS SILICON, I. Mihalcescu, J.-C. Vial and R. Romestain, Laboratoire de Spectrométrie Physique, Université Joseph-Fourier Grenoble, BP 87, 38402 St Martin d'Hères Cedex, France

It is often presumed that the stretched exponential decay of photoluminescence (PL) in porous silicon is a consequence of a variable range hopping of photoexcited carriers between the localized states of the three dimensional silicon sponge structure. In this paper, however, we show unambiguously that carrier hopping in porous silicon is absent in the microsecond time range, from ambient temperature up to 450K. We demonstrate this by comparing resonantly and non-resonantly excited PL decays. The invariance of the decay shape is interpreted in the light of different carrier recombination models.

B-II/P43 STUDY OF THE RECOMBINATION MECHANISMS AND DEFECTS OF POROUS SILICON LIGHT EMITTING DEVICES, S. Lazarouk, Belarusian State University of Informatics and Radioelectronics, P. Browki, 6, 220027 Minsk, Belarus and T. Gorbach, P. Smertenko, S. Svechnikov, Institute Semiconductor Physics of NAS, 45, Nauki Ave. 252650 Kyiv, Ukraine and Y. Boyko, E. Buzaneva, O. Chukova, S. Nedelko, G. Popova, O. Tretyak, T. Shevchenko, Kyiv University, 64 Vladimirska str., 252033 Kyiv, Ukraine, L. Pavesi, INFN and Dipartimento di Fisica, Università di Trento, 14, Sommarive via, 38050 Povo (Trento), Italy

Present light emitting diodes (LED) based on porous silicon and nanocrystalline silicon are not able to yield high external quantum efficiency. We believe that one limiting factor is the lack of detailed knowledge of the recombination mechanisms occurring in these structures. Both quantum confinement and chemical effects contribute to the emission. In order to deepen further the understanding of these complicated systems and to improve present LED devices, we have undertaken a detailed investigations of the nature of the recombination centers and mechanisms. In particular the following questions have been addressed: - the nature and distribution of the recombination centers in porous Si and in nano-crystalline Si through DLTS, XPS, IR spectroscopies; - the nature of the main chemical bonds existing in these centers (XPS, IR spectroscopy); - the peculiarities of the morphology of the interfaces (SPM:SFM, STM); - the relation between the previous results and the LED performances (I-V and EL characteristics).

Characteristic bands (at energies covering the interval 0.45-0.8/0.55 eV) due to the interface or bulk defects states were measured; a defect related with SiO₂ was identified and its excited state with transitions at 4.3 and 2.56 eV was also measured. In addition, it was found that Si microcrystalline the interface with crystalline Si are responsible for EL and it was established a transition regime from monomolecular to bimolecular recombination in the electroluminescence. On the basis of these results new LED structures will be proposed.

B-II/P44 NEW LED STRUCTURES BASED ON POROUS SILICON LAYERS COATED WITH SELF-ASSEMBLED MOX₂-X/C FILMS AND ON MICRO/NANO SILICON HETEROJUNCTION, S. Lazarouk, Belarusian State University of Informatics and Radioelectronics, P. Browki, 6, 220027 Minsk, and T. Mallouk, P. Ollivier, Dept. of Chemistry, The Penn State University, University Park PA 16802 and E. Buzaneva, S. Nedelko, I. Zakharchenko, T. Shevchenko, Kyiv University, 64 Vladimirska str., 252033 Kyiv, Ukraine, N. Kovtyukhova, Institute of Surface Chemistry, 31, Nauki Ave 252028 Kyiv, Ukraine, L. Pavesi, INFN and Dipartimento di Fisica, Università di Trento, 14, Sommarive via, 38050 Povo (Trento), Italy

A model based on the assumption of a concurrent contribution of defects and quantum confined states to the luminescence of low dimensional silicon nanostructures (porous silicon and Si nano-crystals) is presented. It is applied to the study of high electrical injection into layered light emitting diodes. These are formed by a three layers structure: 1) N⁺-type doped semiconductor with energy gap E₁, 2) intrinsic semiconductor with energy gap E₂>E₁, 3) p-type doped semiconductor with energy gap E₃<E₁. In addition the intrinsic semiconductor is characterized by a band of interface and bulk defects. This layer system simulates the porous silicon based LED of Ref. [L. Pavesi et al. Thin Solid Films 297, 272 (April 1997)]. With E₁=1.4 eV, E₂=1.6-2.0 eV and E₃=1.1 eV a fit of the experimental data yields a defect band located at 0.45-0.7 eV with a density of 10¹⁸ cm⁻³. Based on the theoretical results a new LED structure has been realized with the following structure: 1) self-assembled MoxS₂-x/carbon film on porous Si (layered by layer coating with laser illumination); 2) microporous Si obtained by electrochemical dissolution followed by implantation group IV metals (Zn,...) to compensate the residual doping; 3) Si wafer p-type doped. Different structures were investigated through DLTS, XPS, IR spectroscopy, UV and visible absorption, SPM:SFM and STM. The principal characteristics of this layer which were predicted earlier were confirmed. An intense visible EL band, centered at 575 nm and 230 nm wide was observed in the optimized devices for a bias lower than 10 V and injected currents lower the 100 mA.

- B-II/P45** PHOTO-THERMAL CHARACTERIZATION OF POROUS SILICON SAMPLES, U. Bernini, P. Maddalena, E. Massera, A. Ramaglia, INFN Dip. Scienze Fisiche, Università di Napoli, Via Cintia, 80126 Napoli, Italy
The photoacoustic technique is largely used for the thermal and optical non-destructive characterization of materials. For stratified media, such as porous silicon on the bulk substrate, it is possible to determine first the thermal diffusivity of the sample and then, once the diffusivity is known, the absorption spectrum. In order to measure the thermal diffusivity normally one investigates either the frequency dependence of the sample surface temperature (front surface illumination) or the transmission factor (rear surface illumination); alternatively, a comparison can be performed between the photoacoustic signals relative to the two types of illumination. These considerations apply well only when stratified media of simple geometry are studied, otherwise the frequency dependence of the photoacoustic signal can be different from the expected one. This is certainly true for porous silicon samples etched on the bulk silicon substrate: in this case, indeed, the thermal exchange between the coupling gas and the material is different when the front- and back-surface of the sample are considered. In this work is presented a new and alternative method for the measure of thermal diffusivity in porous silicon by considering the photoacoustic response at fixed frequency of samples having the same porosity but different thickness. The analysed samples are fabricated by etching *n* type, 1 Ωcm , 550 μm thick *c*-silicon; they have a porosity ranging from 40 to 70% and thickness from 45 to 250 μm . The measured thermal conductivity is lower than the one reported for crystalline silicon by two orders of magnitude.
- B-II/P46** THE ORIGIN OF PHOTOLUMINESCENCE IN Ge-IMPLANTED SiO_2 LAYERS, H.B. Kim, K.H. Chae, and C.N. Whang, Department of Physics & Atomic-scale Surface Science Research Center, Yonsei University, Seoul 120-749, Korea; J.Y. Jeong, M.S. Oh, and S. Im, Department of Metallurgical Engineering, Yonsei University, Seoul 120-749, Korea; J.H. Song, Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 130-650, Korea
The study of semiconductor nanocrystals embedded in SiO_2 is becoming an expanding field of interest because of their potential as optoelectronic emission devices directly coupled with Si integrated circuits. For a fabrication technique of these nanocrystals, ion implantation may be a good candidate in that it produces a controlled depth distribution of desired species. The SiO_2 layer with a thickness of 300 nm was grown by wet oxidation of Si(100). Ge negative ions were implanted into SiO_2 layer at room temperature (RT) with an energy of 100 keV. The employed doses of Ge-ion were 5×10^{15} , 1×10^{16} , and 5×10^{16} ions/ cm^2 . After implantation, the samples were annealed in nitrogen ambient for 2 hours at various temperatures. X-ray photoelectron spectroscopy (XPS) measurements were performed using a standard Al K α (1486.7 eV) excitation source in an electron spectrometer ESCA 5700 (PHI Ltd.). Photoluminescence spectra were obtained at RT in a conventional way using an Ar-ion laser (457.9 nm) as an excitation source and the detector as a cooled photomultiplier tube. A strong PL around 2.0 eV is observed from as-implanted sample, and after annealing at 900 $^\circ\text{C}$ in nitrogen ambient for 2 hrs, the luminescence disappears. It implies that the luminescence from the as-implanted sample is related to some radiative defects formed by Ge-implantation. However, after annealing at 1000 and 1100 $^\circ\text{C}$ for 2 hrs, the luminescence with the same peak position as that of the as-implanted sample shows up again, and its intensity increases with temperature. Hence, the PL from the annealed sample is regarded as a luminescence emitted from Ge nanocrystals formed at the temperature. XPS analysis for both as-implanted sample and the other samples annealed at 1100 $^\circ\text{C}$ exhibits that the as-implanted sample has only small signal of Ge-O bond while the sample annealed at 1100 $^\circ\text{C}$ shows mainly Ge-Ge bond with small amount of Ge-O bond near the expected range of implanted Ge.
- B-II/P47** DEFECT VS. NANOCRYSTAL LUMINESCENCE EMITTED IN RT AND HOT-IMPLANTED SiO_2 LAYERS, J.Y. Jeong, S. Im, M.S. Oh, Department of Metallurgical Engineering, Yonsei University, Seoul, Korea; H.B. Kim, K.H. Chae, and C.N. Whang, Department of Physics & Atomic-scale Surface Science Research Center, Yonsei University, Seoul, Korea; J.H. Song, Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea
Photoluminescence (PL) from nanocrystalline Si has been a subject of considerable interests due to its potential application in Si-based optoelectronic devices. Ion implantation of Si into SiO_2 is a suitable technique for obtaining such nano-systems in a controlled manner with simplicity, compatibility with integrated circuits. Si ions were implanted into thermally grown SiO_2 film (300 nm) on crystalline Si at energies of 30 to 55 keV, and with doses of 5×10^{15} , 3×10^{16} , 1×10^{17} cm^{-2} at room temperature. Implanted specimens were subsequently annealed in N_2 ambient at 500, 800, and 1100 $^\circ\text{C}$ for 5, 30, 60, 120, 240, and 600 min. The Photoluminescence (PL) experiments were performed at room temperature using an Ar-ion laser (wavelength, 457.9 nm) as an excitation source. PL spectra obtained from samples annealed 4 hours at 500, 800 and 1100 $^\circ\text{C}$ after implanted at a dose of 1×10^{17} cm^{-2} shows that luminescence intensity clearly increases with temperature, and that peak moves from an orange band (580 nm) to a red band (720 nm) after annealing at 1100 $^\circ\text{C}$. Similar red-shift of PL band is observed from the high-dose samples annealed at 1100 $^\circ\text{C}$ for different periods. The most interesting results are shown from samples implanted at an elevated temperature of 400 $^\circ\text{C}$ with a lower energy of 30 keV and a lower dose of 5×10^{15} cm^{-2} . A strong luminescence around 600 nm is initially observed with unaided eye from an as-implanted sample, and then vanishes after anneal at 800 $^\circ\text{C}$ for 30 min. However, red PL band (700 nm) comes up with weak intensity after anneal at 1100 $^\circ\text{C}$ for 30 min. This fact clearly shows that there exist two different origins for luminescence from defects and nanocrystals in Si-implanted SiO_2 . Since the 600 nm band is known as a defect-related band, we presume that hot-implantation tends to introduce even more radiative defects to SiO_2 than RT-implantation does.

E-MRS'98 SPRING MEETING



SYMPOSIUM C

Growth, Characterisation and Applications of Bulk II-VIs

Symposium Organizers

R. TRIBOULET

CNRS/LPSB, Meudon, France

P. CAPPER

GEC-Marconi Infrared Ltd, Southampton, UK

G. MÜLLER-VOGT

University of Karlsruhe, Karlsruhe, Germany

SYMPOSIUM C

Tuesday, June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - CdTe and CdZnTe Growth

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|-------|-------------|-----------|--|
| C-I.1 | 9:00-9:30 | -Invited- | <p>CRYSTAL GROWTH CONTROL OF CdZnTe BY IN-SITU EDDY CURRENT MONITORING, R. Singer, Institute for Defense Analyses, Alexandria, VA 22311-1772, USA</p> <p>During the course of the Infrared Materials Producibility Program - an effort managed by the US Defense Advanced projects Agency and dedicated toward increasing the size and decreasing the cost of CdZnTe wafers - considerable attention was paid to implementing an in-situ eddy current sensor system. Such a system, mounted on both horizontal and Vertical Bridgman furnaces, would improve the single crystal yield of the ingots, by determining the position and concavity fo the meltsolid interface. Initially the sensor was envisioned as a component in a real time closed loop control system, but that effort was supplanted by a more conservative approach wherein the eddy current sensor, mounted on a research furnace, was to provide data to facilitate optimization of growth parameters and to validate computer models. That data, obtained from sensors utilizing both the absolute (single coil) and differential configurations, are presented and discussed in this paper.</p> |
| C-I.2 | 9:30-10:00 | -Invited- | <p>PRE-TRANSITION PHENOMENA IN CdTe NEAR THE MELTING POINT, L. Shcherbak, Institute of Inorganic Chernistry, Chernivtsi University, 2 vul. Kotsiubinskoho, 274012 Chernivtsi, Ukraine</p> <p>The current knowledge about the CdTe melt state is compared with own differential thermal analysis (DTA) and high-temperature (973- 1473K) electrical conductivity measurements (HTEM) in both pure CdTe and doped by ZnTe, in, Ge one. According HTEM data, the CdTe melt retains the semiconductor properties even in donor impurity (In) presence. Thus, the nature of postmelting effect in the CdTe melt is not connected with the type of bonding changes but only with structural reorganisations in the melt.</p> <p>It was concluded, that the CdTe melting and solidification occurs through some steps of structural units transformations. The gradual dissociation of clusters completes near 1390 K (the liquid becomes monostructural). The nuclei formation during melt cooling depends on the initial melt structure. According to DTA data the nucleation and solidification processes may be ruled not only by the melt cooling rate but the rate of solid phase heating also. This is due to the possibility that high-temperature annealing may provoke a phase transition in the solid which results in appreciable melting point value rising (up to 1380 K) in the same specimen. The structural changes caused by thermal fluctuations in the CdTe melt and CdTe-Ge molten alloys are discussed.</p> |
| C-I.3 | 10:00-10:20 | | <p>VAPOR PRESSURE SCANNING IMPLICATIONS OF CdTe CRYSTAL GROWTH, J.H. Greenberg, Dept of Inorganic and Analytical Chemistry, Hebrew University, 91904 Jerusalem, Israel</p> <p>Vapor pressure scanning (VPS) is a direct high precision method of investigation of the composition of non-stoichiometric crystals at high temperatures. It is based on experimental measurements of the vapor pressure, from which three-dimensional P-T-X (pressure-temperature-composition) range of existence of the crystalline phase is outlined. For CdTe the accuracy of the VPS determination of non-stoichiometry was proved to be within 10⁻⁴ at.% for temperatures up to the melting point (1365 K).</p> <p>In this communication it will be shown how to apply experimental P-T-X phase equilibrium data for preparation of the material with a pre-determined composition, either stoichiometric or with a certain deviation from stoichiometry. Different technologies will be analyzed: vapor phase growth, vertical, horizontal and high pressure Bridgman.</p> |
| | 10:20-10:50 | | <p>BREAK</p> |
| C-I.4 | 10:50-11:20 | -Invited- | <p>RECENT DEVELOPMENTS IN II-VI SUBSTRATES, K. Sato and O. Oda, Materials and Components Laboratory, Japan Energy Corporation, 3-17- 35 Niizo-Minami, Toda, Saitama 340, Japan</p> <p>There are many attempts for stable growth of II-VI compound semiconductor bulk single crystals because of their interesting applications in many fields. Recently blue laser diodes and light emitting diodes, which are great interesting in optical recordings and visible displays, have been developed using II-VI materials of a ZnMgSSe system. These diodes have been fabricated on GaAs substrates using hetero-epitaxial growth mainly because it is difficult to obtain high quality substrates of ZnSe for homo-epitaxial growth.</p> <p>In the hetero-epitaxial growth such as ZnSe on GaAs, defects are generated at the interface between substrates and epitaxial layers due to the difference of physical properties of these materials, for instance, lattice constant and thermal expansion coefficient. These defects deteriorate the devise quality and shorten the lifetime. Therefore, high quality substrate for home-epitaxy in II-VI materials are strongly required. However, stable industrial crystal growth methods for most of II-VI materials are under development. There are several attempts to grow the single crystals using novel techniques.</p> <p>In this presentation, recent developments in II-VI material, including present status of II-VI substrates of CdTe, ZnSe and ZnTe and recent topics of newly developed growth techniques of II-VI materials will be reviewed, mainly focusing on the VGF/VB methods for these materials.</p> |

SYMPOSIUM C

C-I.5 11:20-11:40

CdTe AND CdZnTe SINGLE CRYSTAL GROWTH WITH PREDICTABLE AND REPRODUCIBLE MACRO- AND MICROSTRUCTURE, Y.M. Ivanov, Institute of Crystallography of Russian Academy of Sciences, Leninski pr., 117333 Moscow, Russia
Disadvantageous combination of physicochemical properties of CdTe and its alloys makes difficult crystals raising with predictable and reproducible macro- and microstructure. This problem may be solved by Obreimov-Shubnikov method [1] used with combination of self-seeding technique. Based on nucleation on the melt free surface this technique has good reproducibility of free twins single crystals growth in the direction $\langle 111 \rangle$ or $\langle 110 \rangle$ depending on Cd vapor pressure. As opposed to modern tendency, application of the very simple one-zone furnace is possible owing to employment the method of unsaturated Cd vapor pressure creation [2].

The other heavy problem of this materials is Te precipitation. The known methods of overcoming of this phenomenon are not commercial. Mechanism of precipitates nucleation was analyzed within the framework of phases equilibration and kinetic and had been confirmed experimentally. By this model the numerous single crystal ingots in diameter up to 100 mm without polycrystalline starting part had been produced. This materials had not the precipitates which could be detected by methods of infrared or electron microscopy.

[1] I.V.Obreimov and A.V.Shubnikov, Phys. 25 (1924) 31

[2] A.Ya.Nashelsky. Technology of Semiconductor Materials, Moscow, "Metallurgy" (1972) 125 (in Russian).

C-I.6 11:40-12:00

PARAMETERS OF SUBSTRATES - SINGLE CRYSTALS OF ZnTe AND $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x < 0.20$), OBTAINED BY PHYSICAL VAPOUR TRANSPORT TECHNIQUE (PVT), A. Mycielski, A. Szadkowski, E. Lusakowska, L. Kowalczyk, J. Bak-Misiuk, J. Domagala and Z. Wilamowski, Inst. of Physics, Polish Academy of Sciences, Al. Lotnikow 32 /46, 02-668 Warszawa, Poland

Twin-free single crystals of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x < 0.20$) and ZnTe for MBE substrates were grown by PVT method and the process of growth has been optimized. The crystal rods of reproducible quality, 1 inch in diameter, allow us to cut the substrate plates with surfaces parallel to the (100), (110), (111)B, (211)B planes, up to 20mmx20mm in area. To obtain information on the real crystal structure, composition distribution and impurity and defect concentration - the crystals were characterized by: x-ray rocking curve studies and reciprocal space mapping, energy dispersive x-ray fluorescence (EDXRF), photoluminescence measurements at 2 K for both as grown crystals and the crystals baked in cation vapour, reflectivity measurements at 2 K in the region of free exciton, EPR investigations of paramagnetic impurities and the etch pit density measurements. In the paper results of the characterization are presented. For example, impurity concentrations are below 10^{15}cm^{-3} , the free exciton structure is visible in the luminescence spectrum of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ samples baked in the Zn vapour and the width of the rocking curve (FWHM) is 15 - 25 arcsec for the substrate crystals.

C-I.7 12:00-12:20

Zn CONCENTRATION DETERMINATION IN CdZnTe BY NIR SPECTROSCOPY, C.D. Maxey, J.E. Gower, P. Capper, T. Skauli*, GEC-Marconi Infra-Red Ltd, PO Box 217, Millbrook Industrial Estate, Southampton, SO15 0EG, UK.; *Forsvarets Forskiningsinstitutt, PO Box 25, 2007 Fjeller, Norway

Growth of epitaxial layers of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (CMT) onto $\text{Cd}_{1-y}\text{Zn}_y\text{Te}$ (CZT) substrates is widely reported as being performed in order to minimize misfit dislocations at the growth interface. The lattice parameter of CdZnTe alloys with $y \sim 0.04$ are chosen to match that of $x = 0.22$ CdHgTe. However, the rapid rate of change of the lattice parameter, as a function y , means that the uniformity and definition of the required Zn concentration is potentially very critical. Segregation affects in the bulk process means that commercial CZT suppliers are unwilling to accept tight specifications on 'y' and, in addition, different internal techniques and calibrations are being used to determine 'y'. Previously published studies of the non-destructive, near IR assessment of the CdZnTe band edge, required extrapolation techniques to define a cut-on point. Empirically determined correction factors were then applied to account for the affect of substrate thickness variations but no allowance was made for potential variations in the transmission value of the substrate. We report a study of the NIR band edge cut-on, defined by the wavelength corresponding an absorption coefficient (α) - 10cm^{-1} , which automatically corrects for thickness of transmission variations. Data has been correlated against XRD lattice parameter data to determine the required Zn concentration.

12:20-14:00

LUNCH

Tuesday, June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION II - Wide Gaps Growth

C-II.1 14:00-14:20

VAPOUR GROWTH AND DOPING OF ZnSe SINGLE CRYSTALS, Yu. V. Korostelin, V.I. Kozlovsky, A.S. Nasibov, P.V. Shapkin, P.N. Lebedev Physical Institute of RAS, 53 Leninsky pr., 117924 Moscow, Russia

To obtain high perfect conducting ZnSe substrates for homoepitaxy, vapour phase growth and doping experiments were carried out. Important features of the growth in both $\langle 111 \rangle$ and $\langle 100 \rangle$ directions were studied. The improvement of the crystal perfection was based on the following: a) seed selection - small area ($2-4 \text{ cm}^2$) seeds cut from vapour grown crystal with average dislocation density less than 10^4 cm^{-2} were used; b) optimization of the temperature regime to provide the crystal growth in radial and normal directions simultaneously at optimum growth rate of $20-30 \text{ }\mu\text{m/h}$; c) use of the reverse temperature gradient between the seed and the support pedestal to avoid crystal attachment to the pedestal and to minimize the contact area between the seed and the pedestal; d) postgrowth cooling optimization. The doping by In and Al was performed from the vapour phase during the growth process at $T = 1180-1240^\circ\text{C}$. To control transport of the doping element, either Al or In contained material was placed in a special container with calibrated hole. Doped crystals were annealed in liquid Zn with either In or Al addition to decrease a compensation by V_{Zn} . Twin-free ZnSe single crystals of 50 mm in diameter and 15 mm in height were grown. The dislocation density was decreased to $5 \times 10^3 \text{ cm}^{-2}$. Specific resistivity was as small as $5 \times 10^{-2} \text{ }\Omega\cdot\text{cm}$. It was found the decrease of oxygen content in ZnSe single crystals grown in the $\langle 100 \rangle$ direction in comparison with the $\langle 111 \rangle$ one. The obtained ZnSe substrates were successfully used for both MBE and MOVPE homoepitaxy.

C-II.2 14:20-14:40

IN SITU OBSERVATION OF TWIN FORMATION DURING THE GROWTH OF ZnSe SINGLE CRYSTALS FROM THE VAPOR PHASE, E. Schönherr and M. Freiberg, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

Single crystals of ZnSe are grown in closed ampoules of fused silica at temperature between 1300 and 1400 K. In order to find the reason for twin formation the growth of the crystals is observed with a video camera at a resolution of $5 \times 10^{-3} \text{ cm}$. The pictures are stored on a laser. The crystals develop preferably $\{110\}$ faces. The basic twin, i.e. an ortho-twin, is generated at the corner of three $\{110\}$ faces. This repeated twin formation accelerates noticeably the growth and leads the crystals to spread preferably into the $\langle 111 \rangle$ direction. The probability of twin formation decreases slightly with increasing temperatures while the twinning is not affected by an excess of Se_2 or Zn in the vapor phase.

When traces of SiS_2 are added to the ZnSe source material the $\{110\}$ equilibrium form of the ZnSe crystals changes to a cubo-octahedron, and in addition, the twin formation is dramatically reduced.

With an abrupt change of the supersaturation it is possible to determine the critical free energy to be between 0.3 and 0.5 kcal/mol.

C-II.3 14:40-15:00

Al-DOPED ZnSe ORIENTED SUBSTRATES, P. Lemasson, A. Rivière, G. Didier, A. Tromson-Carli and R. Triboulet, CNRS/LPSB, 1 Place A. Briand, 92195 Meudon Cedex, France

High quality n-type ZnSe substrates have been obtained by Al diffusion into bulk crystals from Zn-Al mixture. Two different processes have been implemented: (i) diffusion of Al throughout micrograin ZnSe samples followed by solid phase recrystallization, (ii) recrystallization of micrograin samples followed by Al diffusion. While in the first case the obtained crystals remain small, twinned and presenting an extra luminescence peak at 2 eV, in the second case, twin-free large single crystals ($1.5 \times 1.5 \text{ cm}^2$ or more) are produced whose quality is demonstrated from SIMS analysis, X-ray diffraction rocking-curves and electron microscopy in cathodoluminescence mode. Hall effect measurements indicate a free electron density of $5 \times 10^{17} \text{ cm}^{-3}$ at room temperature.

C-II.4 15:00-15:20

DEPENDENCE OF LATTICE PARAMETER OF MELT-GROWN ZnSe ON Zn PARTIAL PRESSURE DURING IN-SITU ANNEALING, H. Udo, I. Kikuma and Y. Okada*, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanarusawa-cho, Hitachi-shi, Ibaraki 316, Japan; *Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba-shi, Ibaraki 305, Japan

We measured the absolute lattice parameters of annealed ZnSe crystals by the Bond method. ZnSe bulk crystals were grown under argon pressure of 6 MPa in a high pressure chamber by a modified vertical Bridgman method. After solidification, the grown crystals were annealed for 20 hours in-situ in a crucible under Zn partial pressure which was controlled by heating Zn in reservoir. In-situ annealing were carried out by changing the crystal temperature, $T_{\text{ZnSe(A)}}$, from 700 to 1000°C and the Zn reservoir temperature, $T_{\text{Zn(A)}}$, from 450 to 900°C . Specimens for the Bond measurements are prepared by cleaving the crystals, and then the surface was etched by a bromine methanol solution. Lattice parameters were determined from 044 reflection of $\text{CuK}\alpha 1$ (wavelength; 0.15405945 nm) at 25.0°C . The corrections of temperature, reference, divergence and Lorenz-polarization were made at each measurement.

Lattice parameters of annealed crystals at $T_{\text{ZnSe(A)}}=1000^\circ\text{C}$ changed from a value of $0.566902 \pm 0.0000025 \text{ nm}$ in as-grown crystal depending on $T_{\text{Zn(A)}}$. When crystals annealed at low $T_{\text{Zn(A)}} (< 600^\circ\text{C})$, the lattice parameter decreased by $7 \times 10^{-6} \text{ nm}$, whereas the lattice parameter increased by $1.2 \times 10^{-5} \text{ nm}$ at high $T_{\text{Zn(A)}} (> 700^\circ\text{C})$. This large lattice parameter change between low and high $T_{\text{Zn(A)}}$ suggests that the large amount of native defects and/or complex defects with impurities, and/or formation of the complex defects in ZnSe change by partial pressure of Zn during annealing.

15:20-15:50

BREAK

SESSION III - Narrow Gaps

C-III.1 15:50-16:20 -Invited-

LASER EMISSION IN CdHgTe IN THE 2-3.5 μm RANGE, J. Bleuse, J. Bonnet-Gamard, G. Mula, N. Magnea and J.-L. Pautrat, CEA-Grenoble, Département de Recherche Fondamentale sur la Matière Condensée/ SP2M/PSC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Stimulated emission from CdHgTe Separate Confinement Heterostructure waveguides embedding quantum wells as gain medium is studied. We explore the effect of composition grading in the barriers as well as that of using strained quantum wells on the temperature evolution of the laser threshold.

The main effect of barrier grading is to suppress carrier trapping at low temperatures, leading to an improved excitation transfer from the barriers to the quantum wells, and to an intrinsic exponential dependence of the threshold on the temperature. Its dependence on photon energy points out the importance of Auger type non-radiative recombinations. We determine the Auger constant in our structures, and compare them with published data. An exponential dependence of the Auger constants on the band gap, valid for type I heterostructures, is shown.

For the strained quantum well structures, a factor of two reduction of the threshold is obtained, as compared with similar band gap unstrained structures. On the other hand, the characteristic temperature is not affected.

C-III.2 16:20-16:40

CAN PERCOLATION CONTROL DOPING, DIFFUSION AND PHASE SEGREGATION IN (Hg,Cd)Te?, D. Cahen, O. Melamed, I. Riess* and I. Lubomirski*, Weizmann Inst. of Science, Rehovot Israel, *Physics, Technion, Haifa, Israel, **EE Dept., UCLA, Los Angeles, CA, USA

We show that percolation can control semiconductor doping and dopant diffusion. This occurs in $(\text{Hg}_x\text{Cd}_{1-x})\text{Te}$ (MCT) when $x > 0.2$. In MCT the metal sub-lattice is a face-centred cubic one, on which Hg and Cd form a near-ideal random alloy. At $x=0.2$ (0.8) there will be a continuous chain of Hg (Cd) through the bulk sample, i.e., the percolation limits. This can affect dopants for which the interaction with Hg is significantly different from that with Cd. Such a species is Ag. It has as added feature the ability to stabilize the Hg(I) state. Chemical considerations show that in so-called substitutional Ag it is much more likely that Hg is reduced, rather than that Ag is oxidized. Such process will be much less favourable with Cd. This explains that Ag dopes MCT p-type only for $x > 0.2$, i.e. above the percolation limit.

The same interaction leads to the 7 orders of magnitude increase in diffusion coefficient when $x > 0.2$.

A direct outcome of the fast diffusion of Ag in MCT is its ability to equilibrate under relatively mild conditions, suggesting that no Ag concentration gradient can exist in MCT. However the opposite is true. This can be understood by the occurrence of ultra-low concentration phase separation in this system, the formation of a Ag-MCT phase, at < 0.01 at. % Ag. This is the result of a balance between elastic attraction and Coulombic repulsion between the charged dopants. *Prima facie* evidence for the phase separation comes from coulometric Ag titration in and out of MCT. Both percolation-controlled doping and ultra-low phase separation may be more widespread than thought, if one looks for them. Systems that undergo surface segregation would appear to be good candidates for reinvestigation.

C-III.3 16:40-17:00

INFLUENCE OF STRUCTURAL DEFECTS ON LATTICE PARAMETER AND COMPOSITION OF $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ EPILAYERS, N. Mainzer, A. Berner, E. Lyakin, E. Zolotoyabko, G. Bahir and A. Sher*, Technion, Israel Institute of Technology, Haifa 32000, Israel, *Soreq NRC, Yavne 81800, Israel

Structural defects strongly influence electrical properties of II-VI material-based devices. In this paper extended defects and their influence on structural parameters in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers are studied, using direct defect imaging, and precise measurements of lattice constant and Cd concentration, x . $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayers, 10-15 μm thick, with different Cd concentrations, x , were grown by metal-organic chemical vapor deposition (MOCVD), on (211)-oriented substrates of CdTe. Cd concentrations obtained via absolute measurements of lattice parameter, using high resolution x-ray diffraction (HRXRD), have been compared with x -values derived by means of energy dispersive spectroscopy (EDS) in scanning electron microscopy (SEM) and by Fourier transform infra-red (FTIR) transmission measurements. Cd concentrations measured by HRXRD were found to be always higher than the x -values measured by the two other techniques (EDS and FTIR). It was proposed that the difference, Δx , between thus obtained x -values is caused by the presence of extended defects randomly distributed over the layer, which leads to a lattice expansion mentioned. Actually, strong dependence was found between defect density, counted in high resolution SEM images, and Δx . This approach can be used for fast, non-destructive screening of layered and bulk $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ samples by FTIR and HRXRD.

C-III.4 17:00-17:20

GENERATION-RECOMBINATION NOISE AND PHOTO-INDUCED TRANSIENT CONDUCTIVITY IN EPITAXIAL CdHgTe LONG-WAVELENGTH INFRARED DETECTORS, N. Paul, C.M. Van Vliet and S. Mergui, Center for Engineering and Applied Sciences, Florida International University, Miami, FL 33174, USA

Electrical noise measurements have been made in CdHgTe epitaxial layers with cut-off wavelengths of 11 or 12 μm grown by Rockwell Semiconductors at frequencies from 10 Hz to 1 MHz in the temperature range 300K-50K. A HP 3589A analyzer was used in the FFT mode (below 40 KHz) and the analog mode (from 40KHz-1mHz). Below 10 KHz the noise was mainly 1/f. At higher frequencies one or two Lorentzians were visible, with time constants ranging from 10 to 0.1 μs . The temperature dependence was indicative of a trap level of 12 meV. In the given temperature range the samples were mainly intrinsic, with a bandgap about 100 meV. It is surmised that the observed level is a hole-trap, situated above the valence band (12-15 meV) and associated with Hg vacancies. The noise measurements were supplemented with photo-induced current spectroscopy data (PICTS) down to 10K employing a closed-cycle He cryostat and laser radiation in the near IR. Arrhenius plots revealed several very shallow levels with depths comparable to those deduced from the noise data. This work was supported by the Air Force/Wright Lab at Wright Patterson AFB, Ohio.

C-III.5 17:20-17:40

ELASTIC PROPERTIES AND THE DEFECTS HETEROSTRUCTURES OF $\text{Cd}_{1-x}\text{Hg}_x\text{Te}/\text{CdTe}$, I.V. Kurilo, I.O. Rudyj, O.I. Vlasenco, State University "Lviv Politechnic", Bandera Str. 12, 290646 Lviv, Ukraine

The elastic properties and characteristic of misfit dislocations of heterostructures $\text{Cd}_{1-x}\text{Hg}_x\text{Te}/\text{CdTe}$ was estimated: the energy of interfaces between crystals (substrate and epilayer material); the critical thickness for loss of coherency in heterojunction; the elastic strain in the epitaxial system; the average elastic strain of small islands; the critical islands size; the strains in heterostructures caused by the difference of lattice parameters and difference of thermal expansion coefficient; the length of the cracks in epilayers; the displacement of the free edge of the layers; the misfit dislocations spacing; the magnitude of the Burger's vector lying in the different misfit plane; the surface density of the dangling bonds of dislocations.

It is concluded that $\text{Cd}_{1-x}\text{Hg}_x\text{Te}/\text{CdTe}$ heterojunctions cannot be regarded as lattice matched because of the densities of misfit dislocations and dangling bonds at the interface. These defects may play an important role in, or may even dominate, $\text{Cd}_{1-x}\text{Hg}_x\text{Te}/\text{CdTe}$ heterojunction device characteristics.

C-III.6 17:40-18:00

LATEST ACHIEVEMENTS IN THE GROWTH OF LARGE-SIZE $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ SINGLE CRYSTALS WITH HOMOGENEOUS PROPERTIES, V.M. Lakeenkov, V.B. Ufimtsev and N.I. Shmatov, State Institute for Rare Metals, 109017 Moscow, Russia

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (MCT) solid solutions remain a basic semiconductor material for infrared devices. The major trends of bulk crystal technology are increase in size, increase in the structural homogeneity of the main properties and improvement of structural perfection. $\varnothing > 50$ mm homogeneous MCT single crystals have been grown using the modified Bridgman method with constant melt feeding with the solid phase.

This method has been mathematically modeled. For MCT with $x = 0.19-0.23$, ampoule speed has been programmed to ensure constant crystal composition. $\varnothing = 50-60$ mm MCT crystals ($0.19 < x < 0.33$) have been grown taking into account modeling data, and their properties have been studied as functions of growth conditions.

The composition distribution usually has an axial symmetry. The coordination dependence of composition is usually a sinusoidal curve with a cycle of 4-6 mm. The composition scatter across a $\varnothing = 50$ mm crystal is not greater than ± 0.005 mole parts of CdTe.

The structural perfection of the MCT crystals is controlled by the temperature gradient at the crystallisation front and the conditions of cooling from the growth temperature. The dislocation density in $\varnothing = 50$ mm crystals is 10^5 cm^{-2} . The homogeneity of the electrophysical and photoelectric properties of the MCT crystals has been studied and proved to depend mainly on change in crystal composition.

After annealing in saturated Hg vapour, MCT crystals with $x = 0.20-0.23$ have an electron concentration of $(1.5-5) \cdot 10^{14} \text{ cm}^{-3}$, a 77 K electron mobility of $(1.5-3.0) \cdot 10^5 \text{ cm}^2/\text{V s}$ and a carrier lifetime of $> 2 \cdot 10^{-6} \text{ s}$.

C-III.7 18:00-18:20

SEEDLESS THM GROWTH OF $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x \sim 0.2$) SINGLE CRYSTALS WITHIN ROTATING MAGNETIC FIELD, A.S. Senchenkov, I.V. Barmin, A.S. Tomson* and V.V. Krapukhin*, KBOM/Splav Technical Center, Berezhkovskaya nab.22, 121059 Moscow, Russia* "Orion" State Scientific Center, Plekhanov str.2, 111123 Moscow, Russia

The large grain single crystals $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ ($x \sim 0.2$) of 18 - 22 mm long with diameter of 25 mm have been grown in Zona-4 furnace by the THM from Te-solution without seed within a rotating magnetic field of 0 - 6 mT. The mathematical simulation of crystal growth process has been carried out on the basis of unsteady Navier-Stokes and Maxwell equations set. The measured radial and longitudinal composition distributions in crystals are in good agreement with the theoretical results. For crystal grown at $B = 2 \text{ mT}$, the standard deviation of x -value is within the range of 0.003-0.007. The influence of the rotating magnetic field on convection in the solution zone and, consequently, on the radial compositional distribution and the interface shape has been investigated.

Wednesday, June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION IV - Doping, Defects, Diffusion

- C-IV.1** 14:00-14:30 -Invited- DOPING AND CONTACTING OF WIDE GAP II-VI COMPOUNDS, **W. Faschinger**, Physikalisches Institut der Universität Würzburg, Germany
- C-IV.2** 14:30-14:50 ELECTRON-IRRADIATION ENHANCED DISLOCATION GLIDE IN II-VI SEMI-CONDUCTORS, **C. Levade** and **G. Vanderschaeve**, CEMES-CNRS, BP 4347, 31055 Toulouse Cedex, France
 In situ deformation experiments in a transmission electron microscope (TEM) provides a unique way to investigate the dislocation behaviour under applied stress at a microscopic scale. In this study experiments have been performed on ZnS single crystals to get quantitative informations on the influence of electronic excitation on the dislocation movement (cathodoplastic effect).
 TEM analysis reveals that moving dislocations are subjected to a strong lattice friction (Peierls mechanism) even under electron irradiation. Quantitative dislocation velocity measurements demonstrate that the dislocation mobility is strongly enhanced by an electronic excitation, as a result of the lowering of the lattice friction. This is consistent with a radiation-enhanced dislocation glide, due to non radiative recombination of injected carriers at electronic levels associated with dislocations. Our results show conclusively that the observed reduction in activation energy is related to a reduction in the kink formation energy.
 Similar experiments on bulk ZnSe (**R. Triboulet LPSB**, Meudon, France) are in progress, the results of which will be presented at the conference.
- C-IV.3** 14:50-15:10 STUDIES ON THE DIFFUSION OF Zn AND In INTO ZnSe, **R. Hanas**, **E.D. Jones** and **R. Triboulet*** Coventry University, Priory Street, Coventry CV1 5FB, UK, *LPSB, CNRS, Meudon, France
 Studies on the diffusion of both Zn and In have been carried out into bulk grown ZnSe slices as a function of anneal time and at temperatures in the range 650-800°C. The anneals were carried out in sealed silica capsules using various overpressure conditions, including saturated vapour pressure (svp) due to In or Zn alone and repeated with overpressures at svp conditions due to Zn or Se. A radiotracer sectioning technique was used for measuring the concentration profiles.
 Initial results indicate the following:
 1) The profiles due to In, instead of being erfc or Gaussian in shape, are exponential with an approximate \sqrt{t} dependency.
 2) In diffusions carried out under Se overpressure gave a much higher dopant concentration and were also much deeper than for similar profiles obtained under a Zn overpressure.
 3) The material used was Zn rich (53 % atomic) and long anneals under svp conditions due to either Zn or Se produced no measurable change in the stoichiometry.
 4) The profiles obtained using zinc also possessed a similar shape using svp conditions due to Zn and do not agree with previously published results.
 These results will be discussed in detail at the conference.
- C-IV.4** 15:10-15:30 STOICHIOMETRY AND IMPURITY CONCENTRATIONS IN II-VI COMPOUNDS MEASURED BY ELASTIC RECOIL DETECTION ANALYSIS (ERDA), **M. Birkholz**, **W. Böhne**, **J. Röhrich**, **A. Jäger-Waldau**, **M. Lux-Steiner**, Hahn-Meitner-Institut, Festkörperphysik, Glienicker Str. 100, 14109 Berlin, Germany
 Polycrystalline ZnSe will be used in a chemical vapour deposition process for thin-film solar-cell emitter layers. The precursor bulk material was characterised with respect to stoichiometry and impurity concentrations by the ERDA method, for which an experimental set-up is installed at the Berlin Ion Beam Facility ISL [1]. The sample material was irradiated with high-energy Xe projectile ions of about 200 MeV. The energy and time of flight (TOF) of the released sample atoms were detected. In contrast to the Rutherford backscattering technique the measurement of both kinetic parameters enables the separation of different masses not only in thin-films but also in bulk material. ERDA allows the simultaneous depth profiling of heavy and light elements including hydrogen. We found the ZnSe bulk samples to exhibit an oxygen surface contamination of nominal ZnSeO₂ composition and thickness of 27×10^{15} at/cm². An accuracy in stoichiometry, i.e., Zn/Se ratio of better than one percent could be achieved and impurity concentrations could be determined down to the 0.01 percent range. Detection limits of the ERDA technique and its capacity for concentration profiling in II-VI materials will be discussed.
 [1] **W. Böhne**, **J. Röhrich** & **G. Röschert**, 13th Ion Beam Analysis, Lisbon, 1997, Nucl. Instr. & Meth. Phys. Res. B, in press.
- 15:30-16:00 **BREAK**

SYMPOSIUM C

C-IV.5 16:00-16:20

INVESTIGATION OF INDIUM-DEFECT PAIRS IN CdTe BY PAC SPECTROSCOPY, U. Reislöchner, N. Achtziger and W. Witthuhn, Institut für Festkörperphysik, Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

PAC spectroscopy is known to be a powerful method to investigate the trapping of defects at suitable probe atoms. The trapped defects are characterized by an electric field gradient (EFG) measured at the probe nucleus. Here $^{111}\text{In}/^{111}\text{Cd}$ probes were used. Defects are trapped at indium donors but the EFG is measured at ^{111}Cd immediately after the decay of ^{111}In . To recognize a certain trapped defect, it is necessary to know the corresponding EFGs at different temperatures and doping conditions. This information is given in this work on a frequently reported EFG ($\nu_Q=60\text{MHz}$) which is observed at $^{111}\text{In}/^{111}\text{Cd}$ probe atoms in CdTe after Te-rich annealing conditions [1,2], as well as after lithium [1] or silver [2] diffusion. This EFG was assigned to indium A-centers $\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}}$ by Wichert et al. [1]. Here it is shown, that probe defect pairs which are characterized at room temperature by various EFGs (49...60MHz) show in each case the same two well defined EFGs [2] at $T=30\text{K}$. Annealing between 350K and 600K changes the room temperature EFG in the given interval, but does not change the EFGs measured at 30K. Based on this result, the possibility and reliability of an identification of $\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}}$, $\text{In}_{\text{Cd}}-\text{Ag}_{\text{Cd}}$ or similar pairs by measuring an EFG at $^{111}\text{In}/^{111}\text{Cd}$ probe atoms is critically discussed.

[1] T. Wichert, T. Krings, H. Wolf, Physica B 185 (1993) 297

[2] U. Reislöchner, N. Achtziger, M. Rüb, W. Witthuhn, J. Cryst. Growth 159 (1996) 372

C-IV.6 16:20-16:40

POINT DEFECT CHARACTERIZATION OF Zn- AND Cd-BASED II-VI SEMICONDUCTORS USING POSITRON ANNIHILATION TECHNIQUES, G. Tessaro and P. Mascher, Centre for Electrophotonic Materials and Devices, Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada

In this study we investigated the point defect characteristics of II-VI compound semiconductors using positron annihilation techniques, including positron lifetime spectroscopy and Doppler broadening measurements. Experiments were performed as a function of measuring temperature in the range of 20 to 400 K, with or without illumination of the samples. The materials studied include a wide variety of both single and polycrystalline binary, ternary, and quaternary compounds.

The studies of Zn-based binary compounds (ZnO, ZnS, ZnSe, and ZnTe) showed that the primary defects in these materials are neutral divacancies. CdTe, on the other hand, displays a defect lifetime much closer to the value expected for a monovacancy, most likely related to V_{Cd} . Ternary compounds formed by alloying CdTe with either Zn or Se generally exhibit a much longer defect lifetime. In the case of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, the defect profile is insensitive to the Zn fraction for $0.04 \leq x \leq 0.20$.

The effect of Cl doping in CdTe was also considered. This dopant has a dramatic effect on the defect profile and is known to create a metastable defect, similar to the EL2 centre in GaAs. Measurements at low temperatures and with in-situ illumination are in progress to investigate the dynamic behavior of these centres.

SESSION V - Substrate/Layer Relationship

C-V.1 16:40-17:10 -Invited-

SUBSTRATE /LAYER RELATIONSHIPS IN II-VIs, S.J.C. Irvine, A. Stafford and M. Ahmed, North East Wales Institute, Plas Coch, Mold Rd, Wrexham LL11 2AW, UK

The progress of II-VI epitaxial growth has been inextricably linked to the development of II-VI substrates, although alternative substrates have on many occasions been more attractive. This talk will concentrate on the relationships between the epitaxial growth and substrates, including non-lattice matched alternative substrates such as CdTe/sapphire. II-VI semiconductors are surprisingly tolerant of large lattice mismatch but change in ionicity can cause problems with defect nucleation at the substrate layer interface. This is apparent with closely matched systems such as CdTe/InSb and ZnSe/GaAs. Control of VI/II ratio during nucleation has proved to be critical in achieving good nucleation and has influence over the interfacial chemistry. There have been some notable successes with heteroepitaxy such as the CdTe/sapphire growth by MOCVD which is used as substrates for epitaxial growth of mercury cadmium telluride (MCT) for infrared detectors. However, it appears that such lattice mismatched systems will always result in a mozaic structure and devices must be tolerant of this. The best example of a lattice matched II-VI substrate system is CdZnTe for MCT epitaxy but this has not always produced better epitaxial growth than the alternative non-lattice matched substrates. It is clear from this and from the less mature research into ZnSe homo-epitaxy that surface preparation is crucial and high quality bulk substrates are often masked by poor quality surfaces. This remains a major challenge for II-VI substrates and for nucleation of epiaxial growth.

C-V.2 17:10-17:30

CHARACTERIZATION OF CdTe SUBSTRATES AND MOCVD $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ EPI-LAYERS, M. Levy, N. Amir, E. Khanin, A. Muranevich, Y. Nemirowsky and R. Beserman, Physics Department and Dept. of Electrical Engineering, Technion City, 32000 Haifa, Israel

CdTe substrates and the quality of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x \leq 0.1$) epilayers grown by metalorganic chemical vapor deposition (MOCVD) on CdTe substrates, were characterized by Raman scattering photoluminescence (PL) as well as by x-ray double crystal rocking curve (DCRC). At low temperature the Raman spectra indicated that the intensity of the LO phonon was enhanced wherever there was a structural defect. The defect induced enhancement is due to large momentum transfer which enhances the intraband Frolich interaction. In addition, the intensity of the bound exciton (BE) and the intensity of the LO phonon Raman are strongly correlated, the BE peak intensity measured by PL decreases wherever the LO phonon scattering efficiency increases confirming that defect is the origin of the Raman enhancement. The quantitative measure of the structural perfection is related to the ratio between the defect band and excitonic peaks, and correlates with the x-ray full width at half maximum (FWHM) of the layer peak. It is shown that in addition to these parameters, the FWHM of the PB defect band is a useful parameter to determine the quality of the epilayer, and a good correlation is obtained between the different parameters. The effect of zinc partial pressure in the reactor during growth and the reactor design are studied. The results indicate that crystalline imperfection is caused by lattice mismatch between the CdTe substrate and the CdZnTe epilayer and by the nonuniformity of the zinc composition throughout the layers.

POSTER SESSION

17:30-19:30

See programme of this poster session p. C-13 to C-21.

Thursday, June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VI - Nuclear Detection

- C-VI.1** 9:00-9:30 -Invited- **CdZnTe X-RAY DETECTORS: STATE OF THE ART, K.W. Benz** and M. Fiederle, Freiburger Material Forschungszentrum, Universitaet Freiburg, 79104 Freiburg, Germany
During the last 10 years (Cd,Zn)Te has been a favourite material for efficient x-ray detectors for medical and industrial applications. (Cd,Zn)Te shows a higher resistivity up to $10^{12} \text{ Ohm cm}^{-1}$ and higher detector grade ($\mu\text{-products of } 10^{-3} \text{ cm}^2 \text{ V}^{-1}$ for electrons and about $10^{-4} \text{ cm}^2 \text{ V}^{-1}$ for holes) compared to CdTe. Crystals of 70mm in diameter and larger are produced by the High Pressure Bridgman Method. Sophisticated detector systems based on strip and pixel detectors were presented over the last two years. This review will present the state of the art of CZT. By using new growth techniques like a modified Markov method (bulk crystal growth from the vapour phase) crystals of sufficient size and a better quality may be achieved.
- C-VI.2** 9:30-9:50 **ZINC SEGREGATION IN HPB GROWN $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, P. Fougères, L. Chibani*, M. Hage-Ali*, J.M. Koebel*, G. Hennard, A. Zumbichl*, P. Siffert*, EURORAD II-VI s.a., BP 20, 67037 Strasbourg Cedex 2, France ; *CNRS / PHASE, BP 20, 67037 Strasbourg Cedex 2, France**
Recently, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ has become a challenging material for nuclear detection raising hopes for a new generation of room temperature detectors. However, a lot of technical problems are still pending and after a close look one sees that the basic problems found on CdTe are still unsolved. In addition, the presence of zinc makes the crystal growth more complex due to the shape of the ternary phase diagram. Among these problems is zinc segregation. The influence of Zn segregation has already been studied by PL, PIXE and X-ray diffraction but, so far, no clear correlation with nuclear detection has been found. It has been pointed out that zinc modifies the band gap and, therefore, electron-hole pair creation energy. Thus, zinc concentration variations in a device may be a cause of spectrum degradation. Zinc is also a cause of ZnTe precipitation in the crystals as revealed recently by T.E.M. The understanding of zinc behavior in HPB grown CZT crystal is, therefore, of prime importance.
CZT ingots have been grown by the High Pressure Bridgman technique. Zinc concentration has been measured by X-ray fluorescence and PIXE on samples taken from the middle of several wafers cut at different growth positions. The zinc concentration map has been traced for several wafers showing strong discrepancies along the explored areas. The segregation coefficient has been calculated from the experimental data, taking a directional freezing model. A very good fitting with experimental values is obtained, especially, for the PIXE results.
Detectors have been manufactured from the wafers and fully tested in nuclear detection. An experimental correlation appeared between the pulse height of a ^{57}Co spectrum and the zinc content of the starting material. This is supported by the modification of the electron-hole pair creation energy.
- C-VI.3** 9:50-10:10 **INFLUENCE OF DEEP LEVELS IN CdZnTe NUCLEAR DETECTORS, A. Zerrai, K. Cherkaoui, G. Brémond, G. Marrakchi, P. Fougères*, M. Hage-Ali*, J.M. Koebel*, P. Siffert*, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 Av. A. Einstein, 69621 Villeurbanne Cedex, France; *CNRS / PHASE, BP 20, 67037 Strasbourg Cedex 2, France**
Cadmium Zinc Telluride (CZT) gamma-ray detectors show great potential in medical and nuclear material imaging applications. Its high atomic number provide a high absorption, and its high charge carrier mobility enable an efficient charge collection for gamma and X-rays. The total charge collection is related to the mobility-lifetime product of electrons and holes which is strongly influenced by the electrical active defects. These defects act as trapping or recombination centres that decrease the effective charge collection leading to a degradation of CZT detectors performances. Characterization of these levels and understanding of their electrical properties are of great importance in order to control and to improve CZT detection performance. The CZT crystals have been grown by the High Pressure Bridgman technique (HPB). Photo-Induced Current Transient Spectroscopy (PICTS) and Thermo-Electrical Effect Spectroscopy (TEES) have been carried out on several CZT detectors. The results of these measurements and their corresponding nuclear spectrometry are presented and discussed. We have focused our attention on the deep level at $0.90 \pm 0.05 \text{ eV}$ systematically detected in CZT samples. This level may be the possible deep donor level needed to explain the compensation process in semi-insulating CZT materials. A possible correlation between low temperature levels and nuclear detection performances will be discussed.
- 10:20-11:00 **BREAK**
- C-VI.4** 11:00-11:20 **INVESTIGATIONS OF DETECTOR GRADE OF CdTe BY SPACE CHARGE LIMITED CURRENT (SCLC), M. Fiederle, T. Feltgen, K.W. Benz, Kristallographisches Institut, Hebelstrasse 25, Albert-Ludwigs- Universität Freiburg, 79104 Freiburg, Germany**
The application of CdTe as X-ray detectors depends mainly on the high resistivity and the compensation grade of the material. Chlorine is the common dopant to achieve resistivities of 10^8 Ohm cm and higher in normally melt grown material. The compensation mechanism is not really understood up to now.
CdTe crystals were grown by the modified Markov method. The crystals were chlorine ($5 \times 10^{18} \text{ cm}^{-3}$) doped. All samples were single crystals with a length of 20mm and a diameter of 25mm. The crystals showed a resistivity of about 10^8 Ohm cm and a charge collection efficiency of 85% with a bias of 70 Volts. The samples were characterized by optical and electrical methods to correlate compensation mechanism and detection efficiency. The space charge limited current (SCLC) measurements were performed in a temperature range from -20°C up to 70°C .
A deep donor at 0.70 eV was found in all samples. This explained the compensation mechanism by a deep donor in the middle of the band gap. The highest CCE of 85% was achieved in samples where no additional trap could be found. In samples with a low CCE an additional deep level was found at 0.31 eV. This level could be correlate to metal impurities.

SYMPOSIUM C

C-VI.5 11:20-11:40

ELECTRIC FIELD DISTRIBUTION IN CdTe AND $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ NUCLEAR DETECTORS, A. Zumbiehl, M. Hage-Ali, P. Fougères*, J.M. Koebel, P. Siffert, CNRS / PHASE, BP 20, 67037 Strasbourg Cedex 2, France, *EURORAD II-VI s.a., BP 20, 67037 Strasbourg Cedex 2, France

Internal field measurement in nuclear radiation detectors has always been a very difficult task ; it was, generally, estimated through the detection efficiency without any profile indications. A more precise approach was given by the current pulse study through drift velocity measurement ; however, this method suffers from its low accuracy and low signal to noise ratio. Hopefully, II-VI semi-conductors have strong electro-optical coefficients, which allow to make use of the Pockels effect. CdTe and CdZnTe are I.R. transparent and polarized light transmission is strongly related to the electric field inside the device. Therefore, IR transmission provides us powerful tools for electric field mapping.

Several methods based on these effects have been used to measure the electric field profile in different kind of devices. The polarized light source is either a IR laser or an incoherent IR light. The transmitted light is measured by a Si CCD or a Ge photo-detector. A mathematical treatment of the data gives quantitative values for the electric field. THM grown CdTe and HPB grown CZT have been investigated since they are source materials for the detectors. The influence of several geometry is evaluated. Grains boundaries and precipitates influence will be discussed in these pages.

SESSION VII

C-VII.1 11:40-12:00

INVESTIGATIONS ON THE EFFECT OF CONTACTS ON P-TYPE CdTe DLTS-MEASUREMENTS, K. Scholz, H. Stiens and G. Müller-Vogt, Kristall und Materiallabor der Fakultät für Physik, Universität Karlsruhe, Engesserstr. 7, 76128 Karlsruhe, Germany

DLTS-Measurements investigate the defect structure of a Schottky barrier. In polar compound semiconductors like CdTe it can't be ruled out that the original defect structure of the semiconductor material is changed by the contact formation process. For undoped p-type CdTe there is nearly no information on this subject.

As a first step the influences of two Schottky barriers reported in literature, Au and In on $\text{Br/CH}_3\text{OH}$ etched surfaces, on the results of Deep Level Transmission Spectroscopy were investigated. Additionally the I-V characteristics were measured in the temperature working range of the DLTS to determine if the contacts are stable and how they influence the recorded DLTS spectra.

C-VII.2 12:00-12:20

NEGATIVELY CHARGED EXCITON FORMATION IN AN ASYMMETRIC DOUBLE CdTe/(Cd,Mn)Te QUANTUM WELLS, J. Siviniant, N. Paganotto, A. Kavokin, D. Coquillat, D. Scalbert, J.P. Lascaray, J. Cibert*, GES, UMR 5650 CNRS - Univ. Montpellier 2, Place Eugène Bataillon, 34095 Montpellier cedex 05, France; *Equipe CEA/CNRS Microstructures à Semiconducteurs II-VI, CENG 85X, 38041 Grenoble, France

Magneto-photoluminescence and photoluminescence excitation of not intentionally doped thin CdTe/(Cd,Mn)Te single and asymmetric double quantum wells (QWs) revealed a pronounced excitonic transition at the lower-energy side of the peak associated with the neutral exciton. It can be associated with either an exciton bound to a neutral donor (D^0X) or a negatively charged exciton (X^-). Comparing the binding energies of the exciton complexes given in the literature for QWs of different widths, we attributed the low-energy peak to the D^0X complex in single QW and to the X^- state in the wider well of the asymmetric double QW. A X^- binding energy of 3.7 meV has been measured in the wider well separated to the neighboring thin well by a 150Å - thick barrier. The formation of X^- state is favored by the tunnelling of electrons from the thinner to the wider well. Electrons can tunnel, while most of the holes remains trapped in the thin well, because of their heavier mass. The resulting excess of electrons in the wider well provides favorable conditions for the X^- formation. The equilibrium between the three species, neutral exciton, X^- , and electrons, is controlled by tuning the excitation energy and power.

12:20-14:00

LUNCH

Thursday, June 18, 1998

Jeudi 18 Juin 1998

Afternoon

Après-midi

SESSION VIII - Solar cells ; Photorefractivity

- C-VIII.1 14:00-14:30 -Invited-** **STATE OF THE ART AND PROSPECTS OF PHOTOREFRACTIVE CdTe, Y. Marfaing**, LPSB, CNRS, 92195 Meudon Cedex, France
Photorefractivity is an optical phenomenon which allows to create phase holograms in a semiconductor or insulator medium. Such holograms can be used to store, process or transfer optically-coded information. Due to its high electro-optic coefficient CdTe is a good candidate for the study and application of the photorefractive effect in the important near infrared wavelength range. This view has led in the recent years to a number of works devoted to dedicated crystal growth, spectroscopy studies and photorefractivity measurements. The main results will be presented with emphasis on the spectroscopic data relative to the photoactive vanadium impurity and on the physical quantities extracted from two wave mixing experiments. Some optical functions demonstrated using photorefractive Cd(Zn)Te:V crystals will then be described. They are relevant to homodyne detection, determination of laser coherence function and phase conjugated mirrors. All these investigations confirm the potentiality of Cd(Zn)Te as an optimum photorefractive medium in the near infrared. Full realization of this prospect will require to grow large crystals with improved control over incorporation and compensation of the photoactive dopant and reduction of unwanted defects.
- C-VIII.2 14:30-14:50** **INTRINSIC DEFECTS IN PHOTOREFRACTIVE BULK CdTe AND ZnCdTe, H.J. von Bardeleben**, T. Arnoux*, J.C. Launay**, Groupe de Physique des Solides, Universités Paris 6 & 7, UMR 75-88 au CNRS, 2 place Jussieu, 75251 Paris Cedex 05; *3AR/CNRS/Aerospatiale B.P. 11, 33165 St-Médard-en-Jalles Cedex, France; **I.C.M.C.B. Château Brivazac, 33608 Pessac Cedex, France
The electron paramagnetic resonance (EPR) studies of high resistive Bridgman grown bulk CdTe and ZnCdTe single crystals doped with deep donors such as V or Ge have shown, that the electrical compensation must be influenced by the presence of native acceptor and donor defects, which are different from the intentionally introduced dopant[1]. Among them, intrinsic defects such as anion vacancies, cation vacancies and the cation vacancy-shallow donor associated defects - the so-called A-centers - seem to be probable candidates. Intrinsic defects have been observed before by EPR in CdTe, but only after extreme annealing conditions ; examples are the cases of cadmium and tellurium vacancies observed after high temperature annealing or the case of an A-center with a non identified donor observed after neutron irradiation [2]. We report here the observation by EPR of A-centers in Ge doped CdTe and ZnCdTe not submitted to particular annealing conditions. The defect, observed at high concentrations, is attributed to a Ge related A-center, i.e. a cadmium vacancy-second nearest neighbour pair. The defect is photosensitive and electrically active.
[1] H.J. von Bardeleben, V. Mazoyer, J.C. Launay, X. Launay, Semicond. Sci. Technol. 10, 163 (1995).
[2] G. Brunthaler, W. Jantsch, U. Kaufmann, J. Schneider, J. Phys. Cl, 1925 (1989).
- C-VIII.3 14:50-15:10** **CHARACTERIZATION OF PHOTOREFRACTIVE CdTe:Ge, B. Briat**, K. Shcherbin*, F. Ramaz, B. Farid, H.J. von Bardeleben**, Lab Optique, ESPCI, 10 rue Vauquelin, 75231 Paris Cédex 05, France, **Groupe de Physique des Solides, Univ. Paris 6&7, 2 Place Jussieu, 75231 Paris Cedex 05, France
Germanium doped CdTe is known to be an important photorefractive bulk semiconductor[1]. We have measured the photoabsorption as well as the Magnetic Circular Dichroism (MCD) and the Electron Paramagnetic Resonance (EPR) of two samples of different photorefractive properties in order to identify the relevant charge transfer processes. Strong photoinduced absorption changes have been detected for the two samples at ambient and low temperatures (100 K and 4.2 K). They reveal the existence of four absorption bands around 0.95, 1.10, 1.22 and 1.36 eV at 4.2 K. With respect to the situation at thermal equilibrium, the intensity at 4.2 K of the two bands at lower energies decreases under illumination at 0.9 eV while it increases under illumination at 1.3 eV. MCD experiments at 1.4 K have shown non zero signals solely for the two bands at lower energies. Two paramagnetic defects are therefore optically active. EPR shows that one of them is the isolated deep donor $\text{Ge}_{\text{Cd}}^{+}$ [2,3]. A plausible hypothesis for the second is a Ge doping related A-center. A model will be presented.
*on leave from the Institute of Physics, Kiev, Ukraine.
[1] K. Shcherbitt et al., SPIE 2795, 236 (1996); [2] R.M. Bilbe et al., Phys. Stat. Sol. B121, 339 (1984); [3] G. Brunthaler et al., Rev. B31, 1239 (1985).
- C-VIII.4 15:10-15:30** **INVESTIGATION OF DEEP LEVELS IN VANADIUM DOPED CdTe AND Cd_{1-x}Zn_xTe, A. Zerrai**, G. Marrakchi, G. Brémond, R. Triboulet*, Y. Marfaing*, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 Av. A. Einstein, 69621 Villeurbanne Cedex, France; *Laboratoire de Physique des Solides de Bellevue, 1 Place A. Briand, 92195 Meudon Cedex, France
CdTe doped with Vanadium has shown high sensitivity and attractive photorefractive gain at 1.32µm and 1.55µm and is becoming a real promising material for applications in the optical telecommunication. The properties of CdTe bulk materials are controlled and affected by residual impurities and defects. The characterization and control of deep levels are currently important issues. We have studied the electrical and optical properties of V doped CdTe and CdZnTe samples, by a variety of experimental techniques. Photo-induced current transient spectroscopy (PICTS) have been carried out on the as grown samples and deep level transient spectroscopy (DLTS) and deep level optical spectroscopy (DLOS) have been used on Cd-annealed samples. Four main levels are detected at Ec-0.95eV, Ec-0.78eV, Ev+65eV and Ev+0.2eV. We have demonstrated that the capture cross sections for the 0.95eV and 0.78eV electron levels are temperature dependent which is consistent with the multiphonon emission process. The barrier activation energies (E_b) of these levels are deduced. In addition, the σ_n^0 (resp. σ_p^0) optical cross-section spectrum of the 0.95eV trap exhibits a band contribution peaked at 1.15eV (resp. 0.8eV) which could be interpreted as an internal transition of the V^{2+} (resp. V^{3+}) charge state of the Vanadium.

SYMPOSIUM C

C-VIII.5 15:30-16:00 - Invited -

SCIENTIFIC STATUS OF CdTe/CdS SOLAR CELLS, **K. Durose**, P. Edwards and D. Halliday, Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK

Although CdTe/CdS solar cells are the only thin-film materials nearing production readiness, the behaviour of the materials and the mechanisms by which processing influences device performance is not fully understood. Current large area fabrication gives material with a conversion efficiency η of 8-9%, a figure which will have to be improved upon in order for CdTe to remain competitive in the medium term future.

The properties of CdTe and CdS making them suitable for use in heterojunction cells, and preparative methods suitable for industrialisation, will be reviewed. In order to achieve useful efficiencies CdTe cells must be treated by the so-called 'activation' process using chlorine. How these influence doping state, grain growth, junction response and current transport mechanism will be described as far as they are understood at present.

A popular topic for study currently is the interdiffusion of CdTe and CdS which accompanies chlorine activation. Properties of the solid solution, direct measurements of it, and its influence on optical and electrical aspects of the devices will be reviewed.

Recent results using i) EBIC to map carrier concentration near grain boundaries and ii) PL to monitor diffusion and interdiffusion fronts will be presented.

16:00-16:30

CLOSING ADDRESS

END OF SYMPOSIUM C

SYMPOSIUM C

SYMPOSIUM C
POSTER SESSION

Wednesday June 17, 1998
Mercredi 17 juin 1998

Afternoon
Après-midi

Poster Session
17:30-19:30

- C/P1** A DETECTING SYSTEM FOR DOSE MEASUREMENT OF GAMMA- AND X-RAY RADIATION, V.D. Ryzhikov, V.G. Volkov, A.I. Panteleev, V.V. Chernikov, Scientific and Technological Center for Radiation Instruments of STC "Institute for Single Crystals" of the National Academy of Sciences, 60 Lenin Ave., 310001 Kharkov, Ukraine / THE USE OF SEMICONDUCTOR SCINTILLATION CRYSTALS A II B VI IN RADIATION INSTRUMENTS, V.D. Ryzhikov, L.P. Gal'chinetskii, V.G. Volkov, S.N. Galkin, E.A. Danshin, E.K. Lisetskaya, A.D. Opolonin, A.E. Filimonov, V.V. Chernikov, Scientific and Technological Center for Radiation Instruments of STC "Institute for Single Crystals" of the National Academy of Sciences, 60 Lenin Ave., 310001 Kharkov, Ukraine
- C/P2** LUMINESCENCE OF ZnSe(Te) CRYSTALS MELT - GROWN FROM THE CHARGE ENRICHED IN SELENIUM, V.D. Ryzhikov, L.P. Gal'chinetskii, S.N. Galkin, K.A. Katrunov, E.K. Lisetskaya, Scientific and Technological Center for Radiation Instruments of STC "Institute for Single Crystals" of the National Academy of Sciences, 60 Lenin Ave., 310001 Kharkov, Ukraine / EFFECTS OF DEFECT FORMATION ON THERMAL AND RADIATION STABILITY OF SCINTILLATOR ZnSe(Te), V.D. Ryzhikov, N.G. Starzhinskii, STC for Radiation Instruments, Concern "Institute for Single Crystals", 60 Lenin Ave., Kharkov 310001, Ukraine / COMPETITION OF RADIATIVE RECOMBINATION CHANNELS AND ITS EFFECT ON KINETIC AND COUNTING PROPERTIES OF SCINTILLATOR ZnSe(Te), V.D. Ryzhikov, N.G. Starzhinskii, L.P. Gal'chinetskii, S.N. Galkin, E.M. Selegenev, V.I. Silin, STC for Radiation Instruments, Concern "Institute for Single Crystals", 60 Lenin Ave., Kharkov 310001, Ukraine
- C/P3** DISTRIBUTION OF TELLURIUM IN MELT-GROWN ZnSe(Te) CRYSTALS, L.V. Atroshchenko, L.P. Gal'chinetskii, S.N. Galkin, V.D. Ryzhikov, V.I. Silin, N.I. Shevtsov, STC for Radiation Instruments, Concern "Institute for Single Crystals" 60 Lenin Ave., Kharkov 310001, Ukraine
Influence of growth technological parameters (overheating ΔT , inert gas pressure P, crystallization rate V) upon distribution of tellurium dopant was studied for $\text{ZnSe}_{(1-x)}\text{Te}_x$ crystals grown by Bridgman technique in compression furnaces. Values of the "apparent" distribution coefficient of tellurium (K_{Te}) over crystal length were shown to be dependent on ΔT and the related value of charge carry-over ($\Delta m/m$). It was established that at $\Delta m/m = 15\%$ $K_{Te} = 1$; at $\Delta m/m < 15\%$ $K_{Te} < 1$; at $\Delta m/m > 15\%$ $K_{Te} > 1$. This relationship is explained by competition of two processes affecting the distribution coefficient of tellurium: movement to the tail part in accordance with the phase diagram of the ZnSe-ZnTe pseudobinary system and thermal desorption of ZnTe due to its high volatility. Conditions required for preparation of ZnSe(Te) crystals of highly uniform composition are determined.
- C/P4** STRUCTURE DEFECTS AND PHASE TRANSITION IN TELLURIUM-DOPED ZnSe CRYSTALS, L.V. Atroshchenko, L.P. Gal'chinetskii, S.N. Galkin, V.I. Silin, V.D. Ryzhikov, STC for Radiation Instruments, concern "Institute for Single Crystals" 60 Lenin Ave., Kharkov 310001, Ukraine
ZnSe crystals grown from the melt by Bridgman method are characterized by the presence of such microstructure defects as pores and solid-phase inclusions, grain boundaries and packing defects of twinning type. Microstructural and X-ray analysis of the grown crystals has shown that optical non-uniformity is mainly due to coherent twinned interlayers related to the phase transition wurtzite (2H) \rightarrow sphalerite (3C) on cooling which is incomplete over (0001) 2H \parallel (111)3C planes. The tellurium dopant affects favourably the optical uniformity, degree of structural perfection and resistance to cracking of $\text{ZnSe}_{(1-x)}\text{Te}_x$ crystals. This is due primarily to the sphalerite structure being completely stabilized during the growth process and the absence of twinning type packing defects. Concentration of tellurium (x) is determined which is sufficient to make complete the 2H \rightarrow 3C phase transition.
- C/P5** DIFFUSION LENGTH OF MINORITY CARRIERS IN (CdZn)Te AND (HgCd)Te MEASURED BY EBIC METHOD, J. Franc, E. Belas, P. Höschl, P. Moravec, Institute of Physics, Charles University, Ke Karlovu 5, 121 16, Prague 2, Czech Republic, A.L. Toth, Research Institute for Technical Physics, Hungarian Academy of Sciences, Foti ut 56, 1047 Budapest, Hungary and H. Sitter, Institute for Experimental Physics, Johannes Kepler University, Altenbergerstrasse 69, Linz, Austria
Diffusion length of minority electrons and holes in bulk $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x=0.05$) and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x=0.2-0.3$) single crystals produced by the Vertical gradient freezing method ((CdZn)Te) and Bridgman growth from melt of constant composition ((HgCd)Te) were studied. Electron beam induced current (EBIC) images from the scanning electron microscope were used for an evaluation of minority carriers' diffusion length in the temperature range 150-300K. For the collection of excess minority carriers the built-in field of the p-n junction or the Schottky barrier was used.
In the case of (CdZn)Te the diffusion length of electrons in P-type was found within the range 3-10 μm at 300K increasing to $\approx 400 \mu\text{m}$ at 150K. The diffusion lengths at 300K are substantially longer, than those published for pure CdTe. This fact is probably connected with the addition of Zn, which is used to stabilize the crystal lattice or with the method of growth itself.
In the case of (HgCd)Te the diffusion length of minority holes in the N-type samples with the composition $x=0.2$ varies between 30-120 μm at 150 K decreasing with increasing temperature. The diffusion length of electrons in P-type in the same samples varies between 5-10 μm at 150K and this value is increasing with an increasing temperature.

- C/P6** DEFECTS STUDIES IN $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te}:\text{Ga}$ BY DLTS, J. Szatkowski, E. Placzek-Popko, K. Sieranski, Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland and B. Bieg, Institute of Physics, Maritime Academy, Waly Chrobrego, 70-500 Szczecin, Poland.
In $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ gallium is used as shallow donor dopant. However it was found that Ga results in strong photomemory effect in the material [1,2] which is related to the existence of the so-called DX-like centers, in II-VI compounds. In this paper we present the results of our investigation of deep level defects in bulk Ga doped $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te}$ mixed crystals of net donor concentration equal 10^{15}cm^{-3} by DLTS method. In the samples four electron traps labelled by us E1, E2, E3 and E4 have been found. Thermal energy activations related to observed DLTS peaks obtained from Arrhenius plots were equal 0.25eV, 0.45eV, 0.6 eV and 0.94eV. The capture process of electrons from the trap E2 was found to be thermally activated with energetic barrier equal to 0.18eV. The existence of the barrier means that the trap E2 is the candidate to be metastable. From electric field dependence studies of electron emission rates from this trap it was concluded that related defect in its ground state is acceptor-like and the emission of an electron from this state requires a thermal energy activation equal to 0.45 eV. Return to the ground state is possible only after overcoming energetic barrier of 0.18eV height.
[1] N.G. Semaltianos, G. Karczewski, T. Wojtowicz, J.K. Furdyna Phys. Rev.B 47,12540 (1993), [2] J. Szatkowski, E. Placzek-Popko, K. Sieranski, B.Bieg (will be published).
- C/P7** COMPUTER SIMULATIONS - AN EFFECTIVE TOOL IN CdZnTe AND CdHgTe HIGH-QUALITY SINGLE CRYSTAL PRODUCTION, P. Prikrýl, Math. Inst. Acad. Sci., Zitná 25, 115 67 Prague 1, Czech Republic, A. Kalbac, and R. Cerný, Dept. Phys., Fac. Civil Engng., Czech Tech. Univ., Thakurova 7, 166 29 Prague 6, Czech Republic
In optimizing the production of single crystals of semiconducting alloys, computer modeling has become an important tool owing to the fact that computer simulation is much cheaper than many experimental techniques based on the trial and error method. The exact size, geometry and the boundary conditions can be varied effectively without the necessity to use expensive high-purity materials involved in a real experiment. In this paper, examples of the application of computational modeling to the optimization of experimental techniques for the production of CdZnTe and CdHgTe single crystals from the melt, such as the vertical Bridgman method or the vertical gradient method, are presented. In our numerical simulations, the temperature, concentration and velocity fields and the positions and velocities of the moving interface are calculated for various boundary conditions, and the adjustable parameters of the techniques under consideration are optimized. In addition, second-order influences on the mass, momentum and energy transfer, and the effect of uncertainty in the material parameters on computed results are studied. The computational results are compared with the available experimental data.
- C/P8** STRUCTURAL MODIFICATIONS INDUCED IN ZnSe BY SOLID PHASE RECRYSTALLIZATION, E. Rzepka, P. Lemasson and R. Triboulet, CNRS/LPSB 1 pl. A. Briand, 92195 Meudon Cedex, France
Solid phase recrystallization of as-grown ZnSe polycrystals is achieved under various thermal treatments involving different stoichiometric conditions. Relevant color changes in the crystals appear after thermal treatment and/or doping. These optical variations have been measured at liquid nitrogen temperature in the visible and near IR range. Contributions to the color changes are interpreted as due to structural modifications by using light scattering theory. On the other hand, a new absorption band appearing in the near IR at 0.85 eV seems to be correlated to native point defects associated with deviation from stoichiometry induced by thermal treatment.
- C/P9** APPLICATION OF $\text{CdTe}<\text{Cl}>$ CRYSTALS FOR GAMMA-RAY DOSIMETRY, P.M. Tkachuk, V.I. Tkachuk, N.D. Korbutjak, M.D. Raransky, Chernivtsi State University, Kotsjubinski st. 2, 274012 Chernivtsi, Ukraine and D.V. Korbutyak, S.G. Krylyuk, Institute of Semiconductor Physics, NAS of Ukraine, prospect Nauki 45, 252650 Kiev-28, Ukraine
 CdTe -based detectors of nuclear radiation have many practical applications. Nevertheless, the main limitation to their wider use is rather poor energy resolution. To enhance the resolution the hemispherical cooled detectors have been developed. However, it makes difficult to design portable spectrometric devices basing on these detectors.
In this contribution we report on development of the planar CdTe detector with high energy resolution operating at room temperature.
The CdTe crystals were grown by the Bridgman method and doped with chlorine. An improvement of the growth procedure allowed us to obtain the crystals with homogeneous axial distribution of resistivity ($\rho=10^9\text{-}10^{11}$ Ohm.cm at 300 K) and values $(\mu\tau)_e=(0.5\text{-}2.0)\cdot 10^{-3}\text{ cm}^2\text{V}^{-1}$ and $(\mu\tau)_h=(1.0\text{-}4.0)\cdot 10^{-4}\text{ cm}^2\text{V}^{-1}$ for electrons and holes, respectively.
The produced non-cooled planar detectors exhibit the energy resolution less than 2% in the energy range 60-1300 keV. Detailed investigations of detectors were carried out to reveal the influence of detector thickness, applied voltage, and gamma-quantum energy on the resolution.
- C/P10** GROWTH AND CHARACTERIZATION OF HIGH-RESISTANCE $\text{CdTe}<\text{Cl}>$, D.V. Korbutyak, S.G. Krylyuk, Institute of Semiconductor Physics, NAS of Ukraine, prospect Nauki 45, 252650 Kiev-28, Ukraine and N.D. Korbutjak, M.D. Raransky, V.I. Tkachuk, P.M. Tkachuk, Chernivtsi State University, Kotsjubinski st. 2, 274012 Chernivtsi, Ukraine
Application of double-wall ampoules (containing an inert gas or titanium gas-absorber between the walls) was proposed to avoid pollution with carbon while growing CdTe by the Bridgman method.
To increase CdTe resistivity, the crystals were doped with chlorine which was found to promote a self-cleaning of the crystals, i.e. a transformation of electrically active centers into electrically inactive complexes. The optimal concentration of the chlorine impurity $N_{\text{Cl}}=10^{19}\text{-}10^{20}\text{ cm}^{-3}$ was determined.
Detailed investigations of photoluminescence and electrophysical properties of $\text{CdTe}<\text{Cl}>$ crystals were carried out to reveal an influence of growth conditions on the crystal parameters and to optimize the growth procedure. In particular, photoluminescence (PL) spectra of most perfect samples exhibit very narrow lines due to bound exciton recombination and weak impurity-related bands.
As a result, grown $\text{CdTe}<\text{Cl}>$ crystals are characterized by high resistivity (up to 10^{11} Ohm.cm) and high structural perfection, which allows their application as detectors of nuclear radiation.
- C/P11** CONDUCTIVITY CHANGE OF Au/p-CdTe/Au IN DEPENDENCE ON TEMPERATURE GRADIENT, S. Vackova, Department of Physics, Faculty of Mechanical Engineering, Czech Technical University, Technická 4, 166 07 Prague, Czech Republic, K. Zdansky, Institute of RadioEngineering and Electronics AV CR, Prague, K. Vacek, UJEP University, Usti n. Labem, Czech Republic, L. Scherback, P. Feichouk and M. Ilaschouk, Chernivtsy University, Ukraine
Single crystals of p-CdTe with two Au contacts demonstrate large changes of conductivity in dependence on the temperature gradient as it has been shown by the authors in Ref 1. In this work the mechanisms explaining this dependence, the phonon drag effect and the charge redistribution due to the temperature gradient, have been discussed. The change of conductivity reach up to 30% at the temperature gradient of 10K/cm in dependence on the acceptor activation energy. This effect has to be taken into account in proposing semiconductor devices on p-CdTe.
[1] Vackova S., Zdansky K., Scherback L., Feichouk P., Ilaschouk M., Proceedings of XVI. International Conference on Thermoelectrics, August 1997, Dresden, Germany

SYMPOSIUM C

- C/P12** POST-GROWTH CONTROL OF CdTe STRUCTURAL PROPERTIES, N.V. Sochinskii, Dept. Fisica Aplicada and ICMUV, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain and E. Diéguez, Dept. Fisica de Materiales, Universidad Autonoma, 28049 Madrid, Spain.
We review our recent experimental results on the modification of the structural properties of CdTe wafers by the post-growth thermal annealing in different ambients such as a vacuum, a melt of Ga, a vapor of HgI₂, etc. The wafers were cut from the undoped and doped CdTe crystals, which were grown by the vertical Bridgman method, and annealed at a wide range of technological conditions. The effect of the annealing procedures has been studied by numerous structure characterization techniques like synchrotron x-ray topography, FTIR and Raman spectroscopy, cathodo- and photoluminescence.
The post-growth annealing has been shown to produce an important quality improvement of CdTe wafers, revealed by the elimination of Te precipitates and dramatic reduction of other structural defects in the wafer bulk. The mechanisms responsible for the annealing-induced changes in CdTe wafers are considered and the perspectives for further progress in the post-growth controlling of CdTe structural properties are discussed.
- C/P13** HIGH TEMPERATURE CONDUCTIVITY IN THE PHASE TRANSITION REGION, K. Lott and T. Nirk, Tallinn Technical University, Ehitajate tee 5, 0026 Tallinn, Estonia / HIGH TEMPERATURE CONDUCTIVITY IN THE Cu SOLUBILITY LIMIT RANGE IN ZnS:Cu, K. Lott, M. Raukas, Tallinn Technical University, Ehitajate tee 5, 0026 Tallinn, Estonia; A. Vishnjakov, A. Grebennik, D.I. Mendelev University of Chemical Technology of Russia, Miusskaya sq.9, 125190 Moscow, Russia
- C/P14** A METHOD FOR THE CALCULATION OF DEFECT EQUILIBRIUM, K. Lott and L. Tünn, Tallinn Technical University, Ehitajate tee 5, 0026 Tallinn, Estonia
The calculation of the defect equilibrium in ZnS:Cu:Al:Bi:Cl is proposed as example. The high temperature equilibrium of defects is described by a system of quasichemical reactions. The defect model contains as well single point defects as double and triple associated defects. In all 87 defects. The system of equations for the description of the equilibrium contains linear balance equations for impurities and charges and also nonlinear equations for connecting the defect concentrations via equilibrium constants. For the calculation of high temperature equilibrium we find at first the solution for the system of equations of material balance. Then we express the material balance equations via one impurity type of each impurity. Through mathematical substitutions we get an eighth order system of equations with two unknown concentrations. It can be solved by the triple iteration method. For the calculation of frozen-in defect equilibrium we select for calculation purposes all defects into three groups: neutral double and triple associated defects having no charged analog; defects, existing in three different states of ionization; defects, existing in two different states of ionization. Then we express the concentrations of all defects via the total concentration of the same type of defects. To complete the calculation we solve the electroneutrality equation and check the validity of the material balance equations.
- C/P15** IMPROVEMENT OF CdTe SUBSTRATES QUALITY BY ACOUSTIC TREATMENT, V.L. Korchnoi, M.I. Lisiansky, R. Weil, A. Berner, Technion-Israel Institute of Technology, 32000 Haifa, Israel
The growth of undoped homogeneous high-resistivity single crystal of CdTe is a difficult problem still nowadays. Due to the retrograde solid solubility effect the concentration of intrinsic defects and their complexes amounts to 10¹⁷ cm⁻³. These defects and uncontrolled impurities create traps, recombination and scattering centers.
As has been shown elsewhere, acoustic vibrations of moderate level, which don't generate new defects in the material, stimulate the conversion of existing ones, particularly, their dissociation. We subjected undoped p-CdTe to acoustic wave treatment (AWT) in an attempt to convert defects and remove them from the bulk, thus to improve the bulk quality. An experiment of AWT was carried out on samples of different origins, using then AES, SEM and EDS analysis techniques. It was found that: a) after AWT the surface of the material (0.1 μm) was enriched by Te (up to 80% at.) and this enrichment was accompanied by an appreciable change of surface morphology; b) remarkable lines of copper in EDS spectra were found after AWT (Cu concentration in the surface layer is ~0.9%); c) AWT changes at least by a factor of 3-4 the concentration of defects responsible for the bulk conductivity. The results were explained with the assumption that the conductivity is caused by defects containing doubly charged Cd vacancies, and that AWT promotes the transport of mobile defects (V_{Cd} and copper) to the surface. The defects could now be removed by polishing the surface.
- C/P16** LOW PRESSURE SYNTHESIS AND BRIDGMAN GROWTH OF Hg_{1-x}Mn_xTe, C. Reig, N. Sochinskii and V. Munoz, Dept. Fisica Aplicada and ICMUV, Universitat de Valencia, Dr. Moliner 50, 46100 Burjassot, Spain
To avoid high pressure related to high temperature reaction between the components in elemental form, Hg_{1-x}Mn_xTe single crystals have been synthesised and grown by the Bridgman method in the same ampoule (wall thickness 1.5 mm) using HgTe THM-grown crystals together with Mn and Te to complete the stoichiometry of the desired composition. The growth was carried out at temperature in the range of 700-850°C and rate of 1.5-2.5 mm/h. The Hg_{1-x}Mn_xTe crystals have been characterised by X-ray diffractometry, EDAX, FTIR spectroscopy and Hall techniques, and the effect of growth conditions on the crystal properties is analysed. Although the effective distribution coefficient of Mn is found to be in the range of 3-3.5, the crystals show a good axial composition uniformity throughout more than a half of the total length. The lattice parameters of Hg_{1-x}Mn_xTe are reported for the studied composition range of x<0.2.
- C/P17** STUDY OF THE CHEMICALLY ACTIVATED SUBLIMATION OF ZnSe, I. Mora-Sero, V. Munoz, Dept. de Fisica Aplicada, Universitat de València, Edifici d'investigacio, Dr. Moliner 50, 46100 Burjassot, Spain; M. Barbe and R. Triboulet, C.N.R.S., Laboratoire de Physique des Solides de Bellevue, 1 Place Aristide Briand, 92195 Meudon, France
The reactions and processes involved in the growth of ZnSe by chemically activated sublimation in a H₂ atmosphere are studied. The rate of transport as a function of the source and substrate temperatures and the difference between them are determined from close spacing vapour transport experiments. According to this process, ZnSe layers are deposited on sapphire substrates by short distance chemically assisted sublimation. The experimental results are analysed and the thermodynamic constants of the transport are determined using a theoretical model for kinetically controlled processes.
The optical and structural properties of the layers are assessed by photoluminescence, X-ray and SEM microscopy techniques.
- C/P18** WIDEGAP II-VI SEMICONDUCTORS DOPED WITH Mn AS DETECTORS OF IONISING RADIATION, B.V. Shulgin, E.G. Sitnikov, Ural State Technical University, 620002 Ekaterinburg, Russia and V.I. Sokolov, Institute of Metal Physics UB RAS, 620219 Ekaterinburg, Russia
Luminescence spectra of ZnSe:Mn, ZnS:Mn and ZnO:Mn are measured at room temperature under X-ray and weak current electron pulse excitation. There are the intensive luminescence bands for ZnSe:Mn and ZnS:Mn single crystals at 585 nm which are associated with Mn(2+) 4T1-6A1 transitions. For ZnSe:Mn it is firstly discovered a fast decay component of scintillation with the time decay τ~20 ns and that is why ZnSe:Mn crystal may be considered as a very important material for an effective scintillator in conjunction with Si-photodiode for detection of ionising radiation. The mechanism of luminescence excitation is considered to be the Auger defect recombination for which it is very essential the existence of deep donor level splitted off by a Mn impurity from the valence band. Many experimental data confirm the existence of the donor level in different II-VI semiconductors. A resonant character of this process is believed to enable us to understand a too weak Mn(2+) emission for ZnO:Mn in comparison with the intensive intracenter luminescence for ZnSe:Mn and ZnS:Mn.

- C/P19** HIGH TEMPERATURE POINT DEFECT EQUILIBRIUM IN CdTe MODELLING, P. Fochuk, O. Korovyanko, O. Panchuk, Institute of Inorganic Chemistry, Chernivtsi University, 2 vul. Kotsiubinskoho, 274012 Chernivtsi, Ukraine
In order to foresee the CdTe crystals' electric properties at ambient temperature it is necessary to know the concentration of native and foreign point defects (PD), introduced during preparation at high-temperature PD equilibrium conditions. Measured can be only the densities of electronic PD, but their values are determined by the concentrations of atomic PD. These latter can be calculated, using a defined PD structure model.
High-temperature carrier density measurements in pure and In-doped CdTe at controlled $\text{Cd}(\text{Te}_2)$ vapour pressure in the 573-1173 K temperature range were performed. Quasichemical defect reactions (QCDR) constants, proposed by different authors, were used for defect concentrations calculations, based on the full electroneutrality condition. Generally, the existent QCDR constants sets don't allow to obtain calculated carrier density values, corresponding to the measured ones. Some of these sets include unrealistic thermodynamic parameters, so the 1.73 (Nobel), 1.92 (Chern) or 1.38 eV (Smith) values of the CdTe energy gap, far enough from the 1.5 eV (300 K) experimental value. An improved QCDR constants set was elaborated, using computer modelling and iteration procedures in order to obtain the best fit between measured and calculated carrier concentrations values simultaneously for different experimental dependencies.
- C/P20** IV GROUP DOPANT COMPENSATION EFFECT IN CdTe, O. Panchuk, A. Savitskiy, P. Fochuk, Ye. Nykonyuk, O. Parfenyuk, L. Shcherbak, M. Ilashchuk, L. Yatsunyk, P. Feychuk, Institutes of Inorganic Chemistry, Physical Electronics, Chernivtsi University, 2 vul. Kotsiubinskoho, 274012 Chernivtsi, Ukraine
The electric, photoelectric and optic properties of CdTe+Ge (Sn,Pb) crystals, obtained by different techniques were investigated. Strong compensation and stabilization effects were observed: carrier densities as low as $(2-20) \times 10^6 \text{ cm}^{-3}$ (300 K) were measured. Such semiinsulating crystals are transparent ($T=65-68\%$ in a 10-mm thick sample) in the whole 2-25 μm range, very thermostable (no changes after 1 hour annealing at 800°C). Their properties are always reproducible for a defined dopant, independent of the growth technique and crystal's purity level. The peculiarities of these materials' photoelectric properties (temperature and infrared photoconductivity extinguishing, superlinearity of luxamper dependencies) indicate, that doping introduces in the crystal deep centers with strong asymmetric cross section capture values for electrons and holes. Their levels' depth corresponds to following values: Ge: $E_V+0.63 \pm 0.03$; Sn: $E_C-0.65 \dots 0.88$; Pb: $E_V+0.40 \pm 0.03$ eV. The obtained results are explained using an amphoteric behaviour model of IV Group atoms in CdTe in the framework of the dopant self-compensation mechanism, assuming the formation of stable complexes between foreign point defects or foreign and native ones.
- C/P21** MAGNETOOPTICAL STUDIES OF QUATERNARY DILUTED MAGNETIC SEMICONDUCTORS, L. Bryja, M. Ciorga, J. Misiewicz, Wroclaw University of Technology, Institute of Physics, Wyspianskiego 27, 50-370 Wroclaw, Poland; P. Becla, MIT Cambridge, USA
Magneto-optical and magnetic studies of quaternary diluted magnetic semiconductors (DMS) $\text{Zn}_{1-x-y}\text{Cd}_x\text{Mn}_y\text{Te}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ with small manganese mole fraction $x < 0.05$ were performed. Measurements of magnetisation and susceptibility of all samples exhibit paramagnetic like behaviour. Magnetoreflexivity and magnetoluminescence studies were performed at temperatures of $T=2\text{K}$ and magnetic fields $B=0-5\text{T}$. We found that values of exchange integrals of quaternary DMS are proportional to those of appropriate ternaries DMS and their mole content for both conduction and valence bands.
- C/P22** CdZnTe RADIATION DETECTORS, A.A. Melnikov, A.S. Sigov, K.A. Vorotilov, A.Yu. Manokhine, Moscow State Institute of Radioengineering, Electronics and Automation, Technical University, Moscow, Russia
Spectrometric properties of CdZnTe radiation detectors were discussed. Uniform CdZnTe monocrystals with high resistivity were grown by vapour phase technique with the use of high purity polycrystalline CdTe and ZnTe binary compounds.
The samples were cut from crystal bars with the diameter of 50 mm and resistivity from $10^{10} - 8 \cdot 10^{10} \Omega\cdot\text{cm}$. After that they were polished and etched in a selective etching reagent. Electrical contacts were used for measurements of detectors properties.
The estimated value of $\mu\tau$ in the crystals varies from $5 \cdot 10^{-6} \text{ cm}^2\cdot\text{V}^{-1}$ to $5 \cdot 10^{-5} \text{ cm}^2\cdot\text{V}^{-1}$ for holes and from $5 \cdot 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}$ to $8 \cdot 10^{-3} \text{ cm}^2\cdot\text{V}^{-1}$ for electrons. The energy resolution of 6% with the sensitive volume of 0.125 cm^3 was obtained at the line of 59.6 keV ^{241}Am . Detectors with the volume of 1 cm^3 had the resolution of 5% at the line of 662 keV ^{137}Cs . Detectors with the volume of 4 mm^3 showed the 1.5% resolution for α -particles (^{239}Pu).
- C/P23** GROWTH OF CdZnTe MONOCRYSTALS FOR RADIATION DETECTORS, A.A. Melnikov, A.S. Sigov, K.A. Vorotilov, A.A. Davydov, L.I. Topalova and N.V. Zhavoronkov, Moscow State Institute of Radioengineering, Electronics and Automation, Technical University, Moscow, Russia
A growth technique of large, uniform, and high resistivity CdZnTe monocrystals for room-temperature radiation detectors was developed. It is based on free growth from vapour phase on a seeding substrate. Binary compounds of CdTe and ZnTe were used for CdZnTe monocrystal growth. They are placed and heated separately to produce devided flows which are introduced into crystal growing zone where they are mixed before deposition on a seeding substrate. For selective cooling of a crystal a principle of a light guide was used.
Large oriented CdZnTe monocrystals with the volume up to 50.10³ mm^3 and Zn content in the range from 4 to 35 mol.% were prepared. The dislocation density evaluated from metallography was in the range from $5 \cdot 10^3$ to $2 \cdot 10^4 \text{ cm}^{-2}$. All crystals were p-type semiconductors with the resistivity up to $8 \cdot 10^{10} \Omega\cdot\text{cm}$. A fluorimetric analysis at 77K displayed a narrow exciton-luminescence band with the absence of edge and impurity bands that suggests high purity and perfect crystal structure.
- C/P24** CRYSTAL GROWTH OF SrS FROM Te SOLUTION AND THEIR OPTICAL PROPERTIES, H. Kagawa, T. Kato and H. Kanie, Science Univ. of Tokyo, 2641 Yamazaki, Noda, Japan
This paper describes the growth of SrS doped with Te and their luminescence properties. A mixture of SrS powder and Te with molar ratio of 1:3 was charged in a graphite crucible sealed into a quartz ampoule under a vacuum of 10^{-4}Pa . The ampoule was held at 1050°C for 300h. SrS crystals were observed within a solidified Te solution. The crystal size was $40 \times 40 \times 40 (\mu\text{m})^3$, which was three times larger than the SrS source powder. Te concentrations of the grown crystals measured with electron probe microanalysis (EPMA) were varied from 1.6% to 6.8%. SrS:Te showed two peaks at 363nm and 525nm in cathodoluminescence (CL) spectra at room temperature. The peaks did not shift with the variation of the Te concentration. As the Te concentration increased the relative intensity of the 525nm band to that of the 363nm band increased. SrS:Te showed two peaks at 400 nm and 508nm in photoluminescence (PL) spectra at 77K. The band at 400nm showed two peaks in 77k PL excitation (PLE) spectra at 307nm and 325nm and the band at 508nm did at 348nm and 508nm. These features of the PL and PLE spectra do not agree with those have been reported in previous paper such as SrS:Cu, SrS:Pb and SrS:Sb. The two PL emission bands were assigned to the Te isoelectronic trap centers.

- C/P25** STRUCTURAL PROPERTIES OF MOVPE-GROWN ZnSe STUDIED BY X-RAY DIFFRACTOMETRY, ATOMIC FORCE MICROSCOPY AND ELECTRON MICROSCOPY, Q. Liu, H. Lakner, C. Mendorf, E. Kubalek, Gerhard-Mercator-Universität Duisburg, Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany, W. Taudt, K. Heime, Institut für Halbleitertechnik, RWTH Aachen, 52056 Aachen, Germany, M. Heuken, AIXTRON AG, Kackertstr. 15 - 17, 52072 Aachen, Germany
ZnSe/GaAs heterostructures grown by metalorganic vapor phase epitaxy were investigated by high resolution x-ray diffractometry (HRXRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM). A key issue for successful device application of this material system is the reduction of the defect density in epilayers. For this purpose structural properties of ZnSe epilayers such as defects distribution, their microstructure, and the correlation to the thickness of ZnSe epilayers were studied. X-ray diffraction curves indicate a tendency of polycrystalline growth with increasing thickness of ZnSe epilayers, while the lattice structure keeps constantly the zinc-blende structure. In a sample containing a 6 μm ZnSe layer, the symmetric x-ray diffraction curve shows besides the (002) and (004) reflections also the (111), (113), (022) and (224) Bragg reflections. The SEM and AFM images indicate structural defects initially in the pyramid form on sample surfaces. With increasing ZnSe layer thickness the size of pyramids generally increases. Finally the pyramids developed to polycrystalline islands. The STEM bright field images show the formation of misfit dislocations already at ZnSe/GaAs interfaces, which are correlated with the development of pyramid-like hillocks on the ZnSe surface.
- C/P26** ENHANCEMENT OF MAGNETOOPTICAL EFFECTS IN ZnHgMnTe SOLID SOLUTIONS, A.I. Savchuk, V.I. Fediv, V.M. Frasunyak, I.D. Stolyarchuk, Dept. of Phys. Electronics, University of Chernivtsi, 274012 Chernivtsi, Ukraine and P.I. Nikitin, General Physics Institute, 117942 Moscow, Russia
Owing unique magnetooptical properties bulk II-VI-based semimagnetic semiconductors are promising materials for optoelectronic application (modulators, optical isolators, magnetic field sensors). As an example quaternary solid solutions of $\text{Zn}_{1-x-y}\text{Hg}_x\text{Mn}_y\text{Te}$ have been studied in this work. Single crystals with $x=0.5$; $y=0.4$ were grown by modified Bridgman method. For the first time magnetoabsorption spectra and Faraday rotation measurements of the single crystals were carried out. The obtained enhancement of Zeeman spin splitting of band states and giant Faraday rotation are in good agreement with our previous data on ternary $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ and can be explained in framework of strong sp-d exchange interaction between the localized magnetic moments of Mn^{2+} ions and the free-carrier spins. We suggest that the investigated quaternary semimagnetic semiconductors can be used for application as sensitive element of magnetic field sensor operating at 1300 nm. Research is supported by EC within INCO-Copernicus Programme (grant No. ERBIC15CT960820).
- C/P27** ISOTOPICALLY PURE ZnSe CRYSTALS FROM THE VAPOR, R. Lauck and E. Schönherr, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany
For the study of isotopic effects on the phonons [1], the Zn isotopes 64 and 68 have been combined with the Se isotopes 76 and 80. Because of the limited quantities of available materials a loss-free method was developed which allowed synthesis, purification, and crystal growth of ZnSe in the same closed ampoule. For synthesis the respective elements were loaded spatially separated into a quartz ampoule. When the temperatures of Se and Zn were stepwise increased to 600 and 1000°C respectively, a spontaneous synthesis occurred in the vapor phase. In addition, on the Zn surface a ZnSe layer was formed which slowed down the process. The synthesized material was sublimed at about 1050°C. Separate crystals appeared between 800 and 950°C by physical vapor transport in an atmosphere of 200-300 mbar Argon. The strong twinning-tendency favored the growth in $\langle 111 \rangle$ -direction [2]. The sublimation was terminated after 2 to 4 weeks leading to noticeable purification by accumulation of impurities in the residual source. We have obtained rod-shaped crystals up to 8 mm length of yellow-orange to light-green colors. The photoluminescence and the Raman spectra show a distinct isotope effect [3].
[1] M. Cardona, in: Festkörperprobleme/Advances in Solid State Physics, Vol. 34, ed by R. Helbig (Vieweg, 1994), 35.
[2] E. Schönherr, M. Freiberg, H. Hartmann, J. Cr. Gr. 179 (1997) 423
[3] A. Göbel J.M. Zhang, T. Ruf, R. Lauck, M. Cardona, to be published.
- C/P28** PREPARATION OF (001) ZnSe SURFACES FOR HOMOEPITAXY, S. Storm, W. Neumann, Humboldt-Universität zu Berlin, Institut für Physik/Kristallografie, Invalidenstrasse 110, 10115 Berlin, Germany
The quality of epitaxial grown layers is strongly effected by perfection and surface morphology of the substrates used. For preparation of smooth surfaces with as-grown perfection material specific parameters have to be considered to minimize the resulting structural degradation of substrates as much as possible. Therefore, a multiple substrate treatment for (001) ZnSe surfaces was developed including a four-step mechanical polishing procedure, a chemo-mechanically polishing and a final step of chemically polishing. The morphology of the treated (001) ZnSe surfaces was investigated by atomic force microscopy (AFM). After mechanically polishing the surfaces are covered with finest polish ridges, which are smoothed after chemo-mechanically polishing. The resulting average roughness of the surface is smaller than 1 nm and can be maintained even after chemically polishing. High resolution X-ray diffraction topography has been carried out to detect the underlying structural degradation caused by mechanical and chemo-mechanical polishing. The thickness of the damaged layer determined by high resolution X-ray diffraction (HRXRD) rocking curve measurements using 311 reflection (penetration depth ≈ 800 nm) is about 10 μm and can be removed by means of a final chemically polishing step. Subsequently one can conclude, that our multiple substrate treatment provide smooth (001) ZnSe surfaces with as-grown perfection proved by successfully homoepitaxial growth.
- C/P29** OBSERVATION OF EXCITON LOCALISATION IN SOLID SOLUTIONS ZnCdSe:Ni AND ZnSeS:Ni BY ELECTROABSORPTION, V.I. Sokolov, Institute of Metal Physics UB RAS, Ekaterinburg 620219, Russia and V.G. Masurenko, P.S. Il'ichev, Ural State Technical University, Ekaterinburg 620002, Russia
The localisation of excitons in solid solutions $\text{ZnSe}_{(1-y)}\text{S}_{(y)}\text{Ni}$ and $\text{Zn}_{(1-x)}\text{Cd}_{(x)}\text{Se:Ni}$ has been observed by electroabsorption at 4.2 K and 77 K and for y, x within the ranges 0 - 0.2 and 0 - 0.02. The measurements were taken in the range of exponential tail of exciton line at the distance of 3-6 energies of exciton ionisation from the centre of exciton line. The positive peak in electroabsorption spectra due to influence of electric field on exciton line depends on type of solid solutions. For anionic solid solutions the observed peaks are more much stronger than for cationic ones. This difference is a results of very strong localisation of excitons in solid solutions ZnSeS in comparison with ZnCdSe solid solutions. The experimental electroabsorption data confirm earlier photoluminescence results on exciton localisation obtained in the energy interval only of 2-3 energy of exciton ionisation from the centre of the exciton line. We have also observed an influence of an solid solution disorder on Ni [d7e] donor excitons. They are very sensitive to composition of solid solutions both anionic and cationic types. We have proposed a Ni donor exciton recombination model including an idea about an intermediate virtual state which may be one of exciting states of a $\text{Ni}(2+)$ ion d8 configuration.
- C/P30** HEAT TRANSFER SIMULATION IN A VERTICAL BRIDGMAN CdTe GROWTH SYSTEM, C. Martinez-Tomas, V. Munoz, Dept. Fisica Aplicada and ICMUV, Universitat de Valencia, Dr. Moliner 50, 46100 Burjassot, Spain; and R. Triboulet, C.N.R.S., de Bellevue, L.P.S., 1 Place Aristide Briand, 92195 Meudon, France
Modelling and numerical simulations of the growth process have been shown to be powerful tools in order to understand the effects of growth conditions and parameters. In this work a finite element model for the steady-state heat transfer has been employed to analyse the role of ampoule geometry and graphite coating thickness in the crystal growth of CdTe by the Bridgman method. This model takes into account the whole system: furnace temperature profile, air gap between furnace walls and ampoule, ampoule geometry, coating if so, solid and liquid CdTe thermal properties, conduction, convection and radiation of heat and phase change. Results show that the temperature profile of the furnace is very sensitive to the charge. As a consequence, significant differences between the velocity of the ampoule and that of the isotherm determining the solid/liquid phase transition have been found at the onset of the growth.

- C/P31** FEATURES OF OPTICAL FTIR SPECTRA OF SEMIMAGNETIC $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ SINGLE CRYSTALS, A.I. Belogorokhov, Institute of Rare Metals, Leninsky prosp., 156-517, Moscow 117571, Russia, L.I. Belogorokhova, V.A. Kulbachinskii, P.D. Marjanchuk, I.A. Churilov, Moscow State University, Physics Department, Russia
Semimagnetic semiconductors e.g. diluted magnetic semiconductors are solid solutions in which one of a component is substituted for an atom of transition element with non-balanced magnetic momentum. It is known that $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ materials reveal electronic type of conduction while conduction in the case of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ is mainly by holes. Supposedly, in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ natural defects are compensated and it is possible to control defect concentration as well as a type of conduction.
The aim of the work was to investigate optical spectra in the far-infrared region at room and liquid nitrogen temperatures. FTIR spectra of the $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ ($0.01 < x < 0.14$; $y = 0.01$) monocrystals in wave number region of (10-600) cm^{-1} have been measured. Analysis of the FTIR line shape and its dependence on the composition demonstrates the behaviour of optical phonons corresponds to that in ternary solid solution. Besides, a number of additional, new phonon modes have been obtained in low-temperature FTIR spectra of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}_{1-y}\text{Se}_y$ single crystals.
- C/P32** INVESTIGATION OF (Cd,Hg)Te DEFECT SUBSTRUCTURE AND CARRIER CONCENTRATION AFTER LASER TREATMENT, A. Zaginay, B. Kotlyarchuk, Institute of Applied Problems of Mechanics and Mathematics NASU, 3b Naukova str., 290601 L'viv, Ukraine, V. Savitsky, V. Pisarevsky, Institute of Applied Physics LSU, 49 Chuprinky str., 290044 L'viv, Ukraine
Purposeful modification of electrophysical properties of single crystals and epitaxial layers for solid solutions (Cd,Hg)Te is possible under pulse light-beam treatment. Thus, the interconnection between the electrophysical properties variation and the near-surface layer structure defects due to laser treatment, is still urgent problem.
The work deals with the experimental research of concentration profiles of electron-hole states in the (Cd,Hg)Te crystal thin near-surface layers under pulse laser irradiation in the region of fundamental absorption.
It is defined that the dislocation density in the region of thermal laser irradiation influence and the degree of stoichiometry deviation exponentially decrease in depth from the irradiated surface.
The carrier charge concentration profiles in the samples are analyzed the method of field effect in electrolytes used in combination with layer-by-layer etching (the step = 0,5 μm) at a depth of excited layer. The maximum dopant concentration ($N = 10^{18} \text{ cm}^{-3}$) is reached at a fixed depth, that depends on the density of radiation energy.
- C/P33** MODIFICATION OF CdTe SUBSTRUCTURE BY LASER IRRADIATION, A. Zaginay, B. Kotlyarchuk, Institute of Applied Problems of Mechanics and Mathematics NASU, 3b Naukova str., 290601 L'viv, Ukraine, V. Savitsky, V. Pisarevsky, Institute of Applied Physics LSU, 49 Chuprinky str., 290044 L'viv, Ukraine
This paper seeks to carry out a complex of researches concerning the influence of pulse laser irradiation on the single-crystal samples of different crystal orientation with intrinsic defects and on those that are specially doped. On the basis of this researches we will define the regularities of structure formation, dislocation substructure evolution, variation of physical properties for crystals in the working range and predict how to apply the modification method obtained.
The evolution of dislocation substructure on the surface and in depth of laser irradiation influence region on the CdTe crystals is studied. The correlations between the microhardness variation nature, curves of thermostimulated current, low-temperature spectra of photo- and thermostimulated luminescence and laser generated dislocation distribution are defined.
The high temperature (600K) annealing of CdTe:Ag crystals with a surface high density dislocation region formed by laser irradiation, leads to the redistribution of the Ag atom concentration. Practical results: formation of effective dislocation getters.
- C/P34** INVESTIGATION OF PROCESSES OF GROWTH FROM GASEOUS PHASE THE HgTe-CdTe SOLID SOLUTION, N.A. Ukrainets, G.A. Ilchuk, B.J. Datsko, V.O. Ukrainets, I.E. Lopatynsky, State University "Lvivska Politehnika", 12 Bandera Street, 290646 Lviv, Ukraine
Processes of growth in vertical ampule single crystals and epitaxial layers of HgTe-CdTe solid solution by chemical transport reaction are investigated. From theoretical analysis of gaseous phase of $\text{HgTe-CdTe-NH}_4\text{Br(I)}$ system the temperatures of zones of sources $T_{\text{CdTe}} = 730-940 \text{ K}$, $T_{\text{HgTe}} = 670-720 \text{ K}$, temperatures of zones of deposition $T = 650-770 \text{ K}$ and concentrations of transferrer $0,03-0,18 \text{ kg m}^{-3}$ were taken. $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ epitaxial layers with $0,1 \leq x \leq 0,4$ on the (110) and (111) CdTe with width up to 10^{-4} m were grown. The layers had homogeneous composition in direction of growth. Width of connecting region was $9 \cdot 10^{-6} \text{ m}$. From electrophysical investigation it follows that they are similar to ones obtained by the liquid epitaxy method. Composition of impurities was analyzed by secondary ion mass-spectroscopy method.
- C/P35** DEEP IMPURITY LEVELS AND SHALLOW DEFECTS IN CdFeTe CRYSTALS, Yu.P. Gnatenko, I.O. Faryna, R.V. Gamernyk, Institute of Physics of NAS of Ukraine, Prospekt Nauky 46, 252650 Kyiv 22, Ukraine
Low-temperature investigations were made of both optical and photoelectric properties of $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ ($x = 0.0038$) crystals. It allows to obtain the informations concerning on the optical quality of this crystal, a nature their inhomogeneity, to determine of the Fe^{2+} deep impurity centers and singly charged acceptor complexes. The anisotropic character of those complexes was founded which involve of the double charged cadmium vacancy and ionized donor. It was shown that their anisotropy are determined by a nature of donor atom and her position in the crystal lattice (cation or anion site). Taking into account the existence of the real deep impurity centers and acceptor complexes it was suggested the mechanism of arising in this crystal of photorefractive effect. At first time it was indicated on the possibility of arising of anisotropy of photorefractive properties for the CdTe crystals containing 3d-elements which not connected with the anisotropy of electrooptic effect.
- C/P36** SCANNING FORCE MICROSCOPY AND ELECTRON MICROSCOPY STUDIES OF PULSED LASER DEPOSITED ZnO THIN FILMS: APPLICATION TO THE BULK ACOUSTIC WAVES (BAW) DEVICES, P. Verardi, C. Ghica*, C. Gherasim**, M. Dinescu***, N. Nastase**, C. Fluerau***, CNR-Area Ricerca Tor Vergata, Istituto di Acustica, Roma, Italy ; *NIMP, PO Box MG-26, 76 900 Bucharest V, Romania ; **National Institute of Microtechnology, Bucharest, Romania; ***IFA, NILPRD, PO Box MG-16, 76 900, Bucharest V, Romania
New results concerning high crystalline ZnO thin films deposited on Si and Sapphire substrates by laser ablation of Zn targets in oxygen reactive atmosphere are reported. Cross section Scanning Electron Microscopy (SEM) studies clearly evidenced a columnar structure of the layer. As a result of the preparation technique for TEM studies, the film is breaking into separate columnar groups: the ZnO columns observed are 100-500 nm thick, depending on the deposition conditions. The diffraction patterns taken on a large selected area reveal the crystalline hexagonal structure of the ZnO film with $a = 0.324 \text{ nm}$ and $c = 0.5205 \text{ nm}$. The (002) diffraction spot is elongated due to the slope of the diffraction object, that is a confirmation of the fact that the columns are grown along the c-hexagonal axis. Scanning Force Microscopy evidenced the sharp boundaries of different domains from the uniform granular distribution on the surface. Characterization of the films was also conducted to establish their performances as piezoelectric layers in transducers for BAW devices in the GHz range. The insertion and conversion losses and the electromechanical constant were measured using an appropriate set-up.

- C/P37** CHOOSING BULK II-VI SUBSTRATES FOR SEGREGATION-FREE CMT EPILAYERS, S.I. Chikichev, Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, Academician Lavrentiev Avenue 13, 630090 Novosibirsk, Russia, and Department of Semiconductor Physics, Novosibirsk State University, Pirogov Street 2, 630090, Novosibirsk, Russia
Epitaxial growth technologies of virtually any multicomponent semiconductor alloy are plagued by almost unavoidable tendency of different crystal components to segregate making all heterointerfaces nonabrupt in principle. Although very fundamental thermodynamic factors are behind this often undesirable behavior it is sometimes possible to alleviate the problem by various kinetical tricks. All these solutions, however, are case-specific and not universal. In the present work I suggest to use the phenomenon of pseudomorphism in fighting out segregation. Very simple thermodynamic model is used to predict bulk CdZnTe or CdTeSe lattice constant which help to suppress segregation in a single CdHgTe pseudomorphic epilayer as a function of layer composition, orientation and temperature. Despite its simplicity the model is able to guide the grower in using the nonhydrostatic strains as a powerful and universal tool in segregation control.
The present work is supported by Ministry of Education of Russian Federation under the program "Integration" through the Novosibirsk State University.
- C/P38** DIRECT EXPERIMENTAL EVIDENCE OF THE SELF-COMPENSATION MECHANISM IN II-VI's, U. V. Desnica, I. D. Desnica-Frankovic, R. Boskovic Institute, Bijenicka c. 56, Zagreb, Croatia, and R. Magerle and M. Deicher, Fakultät für Physik, Universität Konstanz, 78434 Konstanz, Germany
CdS single crystals were implanted with radioactive ^{111}In and stable ^{115}In in $10^{16}\text{--}10^{20}/\text{cm}^3$ total In concentration range at peak maximum, and analyzed with Perturbed Angular Correlation (PAC) and Hall effect measurements. Strong correlation was observed between the dynamics of electrical self-compensation and the formation of $(\text{In}_{\text{Cd}}\text{--V}_{\text{Cd}})$ pairs with thermal annealings. It is shown that the presence of In donors during thermal treatment under S pressure provokes spontaneous formation of (doubly) ionized cation vacancies, $[\text{V}_{\text{Cd}}]$. The concentration of these native acceptors is self-regulated and dependent directly on In concentration, $[\text{In}]$. $[\text{V}_{\text{Cd}}]$ always reaches circa $[\text{In}]/2$ for the whole range of $[\text{In}] = 10^{16}\text{--}10^{20}/\text{cm}^3$. During cooling, these vacancies and In donors form pairs, $\text{In}_{\text{Cd}}\text{--V}_{\text{Cd}}$ (A center), which compensate the rest of donors, leading to highly resistive material. Presented experiments are direct experimental evidence of the basic principle of self-compensation: doped crystals spontaneously creates just a matching concentration of native point defects needed to completely electrically compensate foreign doping atoms. Formation of compensating V_{Cd} vacancies can be completely suppressed up to at least $[\text{In}] = 10^{19}/\text{cm}^3$ by appropriate annealing conditions under Cd pressure. Based on similarities between CdS and other wide-band, highly ionic semiconductors and on conceptual analogy with even more ionic I-VII compounds, we argue that presented microscopic picture of the compensating defect is most likely valid also for the majority of II-VI's doped with In and other group-III donors.
- C/P39** RESISTIVITY SIMULATION OF CdTe AND CdZnTe MATERIALS, A. Zumbiehl, P. Fougères*, M. Hage-Ali, J.M. Koebel, P. Siffert, A. Zerrai**, K. Cherkaoui**, G. Marrakchi**, G. Brémont***, CNRS/PHASE, BP 20, 67037 Strasbourg Cedex 2, France, *EURORAD, BP 20, 67037 Strasbourg Cedex 2, France, **L.P.M., INSA Lyon, Bat. 502, 20, av. A. Einstein, 69621 Villeurbanne, France
Defects and the relations with the levels introduced in the bandgap are among the toughest remaining problems in II-VI semiconductors. Up to now, more than 30 levels have been detected in CdTe and CdZnTe without any clear identification and assignation for most of them. Interaction between all these levels gives the particular electric properties of each sample. In addition, the high resistivity of these materials makes the defect spectroscopy especially difficult. Three electrical methods are well suited for such investigation: PICTS, TSC and TEES. A very useful complement is provided by numerical simulation of some properties and the comparison between calculation and experimental results.
We have used a simple existing model based on the charge neutrality equation and the Fermi-Dirac distributions. This model was improved to introduce more than 3 levels which is largely our case (30 levels, 5-6 Bands). Free carrier concentrations and resistivity at room temperature are then deduced. PICTS and TSC results are used as model input. Results and compensation processes are discussed.
- C/P40** NUMERIC SIMULATION OF VERTICAL BRIDGMAN CRYSTALLISATION OF $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ MELTS, V.M. Lakeenkov, V.B. Ufimtsev, N.I. Shmatov and Yu.F. Schelkin, State Institute for Rare Metals, 109017 Moscow, Russia
 $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid solutions are an important semiconductor material for matrix IR photodetectors and γ -detectors. A number of technological parameters should be controlled in order to obtain perfect single crystals with desired electrophysical and optical properties. In this work, the Bridgman growth of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ melts was mathematically simulated in order to study the regularities of thermal field formation in the melt-crystal system as functions of basic technological parameters, such as ampoule speed, melt diameter and height, and heater size.
The conjugated problem of thermal fields in the melt-crystal system has been considered. Liquid phase thermal convection has been described using the Navier-Stokes equation in the dimensionless Bussinesk approximation for the flow-swirl transient functions. The solid and liquid phase temperature distributions have been determined using the convective heat conductivity equation with account of the Stefan interface condition. The calculations have been performed in the quasi-steady-state approximation, i.e., the ampoule speed has been taken into account only under the Stefan condition to determine interface shape and position.
Numeric solutions have been obtained for the following growth conditions: crystal diameter and height 10-80 mm and 6-12 cm, respectively, quartz ampoule thickness 3 mm, heater diameter and height 9.3 and 63 cm, respectively, and ampoule speed 0.5-3 mm/h. The melt temperature was 1100-1120 °C.
 $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ single crystals with $x = 0.04\text{--}0.08$ have been grown taking into account the results of numeric simulation. The dislocation density in these crystals was $\leq 5 \cdot 10^4 \text{ cm}^{-2}$.
- C/P41** FEMTOSECOND DYNAMICS OF SEMICONDUCTOR II-VI MICROCAVITY MODES, E.A. Vinogradov, A.L. Dobryakov, Yu.E. Lozovik, Yu.A. Matveets, V.M. Farztdinov, Institute of Spectroscopy, Troitsk, Moscow Region, 142092 Russia, and S.A. Kovalenko, Humboldt - Universität zu Berlin, Germany
Dynamics of semiconductor microcavity modes was investigated by femtosecond laser spectroscopy. The change of reflectivity of the ZnS thin films on thick Ni film on quartz substrate under the pumping at $\hbar\omega_{\text{pu}1} = 2.75 \text{ eV}$ and $\hbar\omega_{\text{pu}2} = 5.5 \text{ eV}$ was monitored in wide spectral region 1.6 - 3.2 eV. For the first pumping energy the laser pulse excites electrons of metal (i.e. boundary of the microcavity) and of ZnS layer (by two-photon absorption). Nonequilibrium carriers of metal penetrate through Schottky electron barrier into the semiconductor. For the second pumping energy the pumping pulse is practically totally absorbed in ZnS layer and creates hot carriers in semiconductor. The differences in the processes of carrier excitation lead to quite different changes in dielectric functions of ZnS and Ni and to the differences in the change of cavity modes.
- C/P42** PHOTOPLASTIC EFFECT IN ZnS, S. Koubaïti*, C. Levade and G. Vanderschaeve CEMES-CNRS, BP 4347, 31055 Toulouse Cedex, France. (*) present address: Université Ibn Tofail, Kenitra, Morocco
At variance with III-V compounds, II-VI compounds exhibit a so-called positive photoplastic effect (PPPE), characterized by an hardening of the crystal under illumination with a wavelength close to the band absorption edge. To get a better understanding of this effect, we have performed room temperature Vickers indentation tests on the (001) faces of ZnS single crystals, in darkness and under illumination: We have studied the spectral dependence of the Vickers hardness as well as the evolution of the defect microstructure in the plastic zone around the indents.
Light illumination induces in ZnS a positive photoplastic effect, characterized at a macroscopic scale by an increase of the Vickers hardness. The spectral dependence of Vickers hardness compares well with the spectral dependence of flow stress, as determined by compression experiments. It is suggested that the PPPE originates from a light-induced lowering of the dislocation mobility, as evidenced by a decrease of the length of the dislocation rosette arms. This could be accounted for by a light-induced increase of the electrostatic charge of moving dislocations, resulting in an increase of the Peierls barrier.

- C/P43** PHOTO- AND X-RAY SENSITIVE HETEROSTRUCTURES BASED ON CADMIUM TELLURIDE, R. Ciach, M.V. Demych*, P.M. Gorley*, Z. Kuznicki**, V.P. Makhniy*, I.V. Malimon*, Z. Swiatek, Institute for Metallurgy and Materials Science, Polish Academy of Science, 25 Reymonta St., 30-059, Cracow, Poland; *Chernivtsi State University, 2 Kotsyubynsky St., 274012 Chernivtsi, Ukraine; ** CNRS, Laboratoire PHASE (UPR 292), BP 20, 67037 Strasbourg Cedex 2, France
The heterojunctions (HJ) with CdTe as one of the components are of great scientific interest for application as detectors of optical and ionizing radiation. It is caused by the optimal band gap width ($E_g=1.5$ eV) for transformation of solar energy into electric and by high atomic number ($Z=50$) of cadmium telluride.
The authors have obtained and studied HJ with two types of optic windows – semitransparent metal layer or semiconductor with wider band. Metal-CdTe contacts were created by thermal spread of golden films on fresh-etched or modified (after oxygen or lithium diffusion) surface of crystals with electronic conductivity. Anisotropic HJ were made using reactions of solid phase substitution on the base of n-CdS and p-ZnTe monocrystals.
All HJ studied are sensitive to light and X-ray irradiation and their parameters and characteristics are greatly depend on the type of diode structure and conditions of its growth. The maximum values of the phototransformation efficiency coefficient at 300K under illumination by AM2 are 6%, 9% and 11% for nCdTe-pZnTe, pCdTe-nCdS and Au-CdTe respectively. The temperature coefficient of efficiency changes is about $2.5 \times 10^{-2} \% K^{-1}$. This value is approximately four times smaller than the same for silicon solar cells. It is necessary to emphasize higher radiative stability of CdTe in comparison with Si. The dose sensitivity of CdS-CdSe HJ with p-i-n structure for the stream of X-ray quanta with energy of 8-33 keV is $3 \times 10^{-5} A \times P^{-1}$ hour at 300K.
The ways of structure exploitation parameters improvement are still being considered.
- C/P44** VOLUMETRIC CHANGES AT THE MELTING POINT AND KINETIC PROPERTIES OF CADMIUM AND MERCURY TELLURIDES MELTS, V.M. Glazov, L.M. Pavlova, Moscow Institute of Electronic Technology (Technical University), Physico-chemical Department, 103498 Moscow (Zelenograd), Russia
Dependencies of specific volume of cadmium and mercury tellurides on the temperature were investigated as in liquid, and in solid states by the gamma-radiation attenuation and pycnometric methods [1].
It is shown, that pure CdTe is increases in volume on the melting, and HgTe melts as water-like type, that is with the compression.
The abnormal character of temperature dependence of specific volume of mercury telluride in a liquid phase is marked. The change of volumetric properties of investigated substances is analysed on the basis of Clausius - Clapeyron equation. The calculation values of baric coefficients of the melting temperature for these substances are compared to data of other thermodynamic researches. Kinetic properties of cadmium and mercury telluride melts such as the electrical conductivity, the viscosity and diffusion coefficients were investigated. The results are analysed on the basis of the theory of an activated complex [2] and is established its correlation with data of researches of volumetric properties.
[1] V.M. Glazov, M. Vobst, V.I. Timoshenko Metody issledovaniya svoystv zhidkikh metallov i poluprovodnikov, Metallurgiya, Moscow, 1989.
[2] S.Glasstone, K.J.Laidler, H Eyring. The theory of rate processes. Frick Chemical Laboratory, Princeton University. First Edition, Second Impression. New York and London. 1941.
- C/P45** DIFFUSION IN CdTe AND CdS AND THE PHASE DIAGRAM OF THE CdS-CdTe PSEUDO-BINARY ALLOY, G.J. Conibeer, D.A. Wood, D.W. Lane, K.D. Rogers, Dept of Materials and Medical Sciences, Cranfield University at Shrivenham, Swindon SN6 8LA, UK; P. Capper, GEC Marconi Infra-Red Ltd, Southampton, SO15 0EG, UK
The diffusion of S, O, N and Cl in CdTe and of Te, O, N and Cl in CdS is being investigated over a range of temperatures around 450°C. Diffusion in both single crystal and thin film material is being studied. Diffusion profiles are measured by Secondary Ion Mass Spectrometry, Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis. Results to date for single crystal CdTe S show that $D_0=1.3 \times 10^{-8} cm^2 s^{-1}$ and $Q=1eV$ (from 450-550°C). Data for the other systems described will be presented.
The phase diagram of the CdS-CdTe pseudo-binary alloy has been plotted from 700 to 1000°C, and the Vegard coefficients for the system measured to a greater degree of accuracy than previously. Samples are equilibrated at 1000°C and slowly cooled to the required temperature. X-ray diffraction then gives their phase and lattice parameter. The phase diagram down to 400°C both with and without Cl will be presented.
This system is of interest for thin film CdS/CdTe solar cells. Their performance is critically affected by interdiffusion, phase changes and the presence of O, N and Cl at the heterointerface during processing at 450°C.
- C/P46** INFLUENCE OF HIGH TEMPERATURE ANNEALING IN Bi-AND Sb-BASED MELTS AND VAPORS ON THE DEFECT DISTRIBUTION IN ZnS SINGLE CRYSTALS, V. Korotcov, K. Sushkevich, R. Sobolevskaya, L. Bruk, M. Nazarov, P. Ketrush, State University of Moldova, A.Mateevich street 60, MD2009, Chishinau, Moldova
Photoluminescence (PL) (77-520K) and color micro-cathodoluminescence (CCL) (300K) of ZnS crystals annealed at 1200-1400K in Bi, Zn and Sb melts and vapors were studied. It was shown that thermal treatment in the Bi and Sb containing mediums leads to the appearance of radiation in the green region of the spectrum (530-540nm). The presence of both intracentered luminescence mechanism in Bi^{3+} ions as well as recombination one, stipulated by the nature of Bi ions closest surrounding in the ZnS lattice, is supposed. By using PL and CCL it was established, that annealing in Bi and Sb melts is accompanied by a sulfur and V_{zn} concentration in the region close to the surface, which was in contact with the melt. The influence of the inherited V_{zn} and V_S defects on the formation of PL spectra of annealed crystals was shown. The diffusion mechanism leading to the appearance of the defects responsible for radiation is discussed.
- C/P47** USE OF NEAR INFRARED AS A SCREENING TECHNIQUE FOR CdZnTe SUBSTRATES, J. Gower, C. Maxey, P. Capper, E. O'Keefe, L. Bartlett, S. Dean, J. Harris, GEC-Marconi Infra-Red Ltd, PO Box 217, Millbrook Industrial Estate, Southampton, SO15 0EG, UK. T. Skauli, Forsvarets Forskiningsinstitut, PO Box 25, 2007 Kjeller, Norway
Lattice matching of substrates to layers for epitaxial growth is important in order to reduce misfit dislocations at the growth interface. CdZnTe substrates are the most common choice of material for CdHgTe growth as they strengthen the lattice as well as providing lattice match. However, zinc uniformity across the substrates is still an issue of concern. A new technique for measuring the zinc distributions in CdZnTe substrates, using a $10cm^{-1}$ NIR cut on* has been developed. Practical aspects of this technique, including vertical mounting of samples, will be discussed. The results of measurements performed on CdZnTe substrates from a variety of sources will be presented. In some instances these results have been correlated with XRD and PL data.
The above techniques have also been applied to CdTeSe substrates from various sources. Because of segregation effects during bulk crystal growth CdZnTe substrates are, in general, less uniform than CdTeSe substrates.
*C. Maxey et al, This conference.

C/P48 [GaAs]_x[ZnSe]_{1-x} RERADIATING LAYERS ON GaAs/Ge SOLAR CELLS, V. A. Krasnov, Inst. of Semicond. Phys., Ukrainian Acad. Sci., Kherson Depart., PO Box 76, 325008 Kherson, Ukraine

Considerable increase of GaAs and AlGaAs solid solutions solar cells efficiency, in particular, it may at the expense of their photosensitivity spectra widening into the short-wave part. Deposition of thin [GaAs]_x[ZnSe]_{1-x} reradiating epitaxial layers, which possess of high quantum radiation efficiency, on the photosensitive heterostructure surface of solar cell is a perspective method of practical realization of it [1]. Discounting the constant extension of GaAs/Ge solar cell's application, the elaboration of such cells with [GaAs]_x[ZnSe]_{1-x} reradiating layers is interesting.

For investigations n+Ge:Sb(substrate)/nGaAs:Se/pGaAs:Zn/p+AlGaAs:Zn (optical window) solar cells heterostructures were used. Unlike the method [1] in present work thin layers ($\leq 0.5 \mu\text{m}$) of [GaAs]_x[ZnSe]_{1-x} solid solutions ($x=0.01\dots 0.15$) deposited on heterostructure surface by sandwich-transfer GaAs and ZnSe molecules from the specially prepared planar source in hydrogen flow to "is not far disposed" substrate method.

The parameters of solar cells (2,3x2,3cm) are produced on the base of heterostructures with the reradiating layers in conditions of AM1,5 at 28°C were following: short-circuit current density $I_{SC} = 22.0\dots 22.5 \text{ mA/cm}^2$ cell's efficiency 24,4...25,2%, while without reradiating ones: $I_{SC} = 17.5\dots 18.2 \text{ mA/cm}^2$, cell's efficiency 19,3...20,2%. Open-circuit voltage both heterostructure types $V_{OC} = 1.045\dots 1.050 \text{ V}$.

These results demonstrate the efficiency of [GaAs]_x[ZnSe]_{1-x} reradiating layers application into GaAs/Ge solar cell's construction.

[1] A.M.Demchenko, V.A.Krasnov. Zhurn. Prikl. Spectros.48, 793 (1988).

C/P49 INVESTIGATION OF THE GRAIN GROWTH IN THE SOLID STATE RECRYSTALLIZATION OF ZnSe, S. Fusil, A. Zozime, A. Rivière and R. Triboulet, Lab. Phys. des Solides de Bellevue, 1 Place A. Briand, 92195 Meudon Cedex, France

Low temperature growth of ZnSe by Solid State Recrystallization has been used to avoid the phase transition in the solid state where a very high density of twins is induced. Furthermore, contamination from the environment during the high temperature melt growth is also avoided.

We started from polycrystalline ZnSe obtained by Chemical Vapor Deposition. The grain diameter lied between 10 and 100 μm . Isothermal annealings were performed in ampoules in which a charge of selenium or zinc was introduced in order to define the nature of the annealing atmosphere. The samples were annealed for 16 h up to 432 h, at 1000°C, under a pressure of 5 atm or 2.1 atm respectively for Se and Zn. The measurement of the mean grain diameter D, gave a growth law of the form $D=kt^{1/n}$ as in the case of metals, where t is the annealing time. The value of 1/n is about 0.24 and 0.06 respectively under Se-rich and Zn-rich conditions. A secondary abnormal growth took place in samples annealed at 700°C under a Se-saturated vapour pressure while grain growth was not observed under Zn-saturated vapour pressure. Those results show the influence of the annealing atmosphere on the grain growth kinetics, which can probably be connected to the nature of the point defects present in each of the samples. An investigation of the evolution of the grain orientations for different annealing conditions is in realisation with Electron Channeling Pattern and will be compared with the initial (111) texture.

C/P50 EFFECT OF DISLOCATIONS ON CRYSTAL STRUCTURE AND CHARGE STATES OF PARAMAGNETIC CENTERS IN ZnS, M.F. Bulanyi, V.A. Kovalenko, S.A. Omelchenko, Diepropetrovsk State University, Radiophysical Department, 13, Nauchnaya by Street, Diepropetrovsk, 320625 Ukraine

By ESR method the effect of plastic deformation of ZnS and ZnSe crystals on the crystal structure, symmetry of Mn^{2+} centers and change of charge states of photosensitive Cr^{2+} and Fe^{2+} centers.

Zinc sulfide crystals of microtwin and polytype structures (6H, 4H) have been shown to undergo the structure transition during plastic deformation ending with the complete reorientation of the specimen structure into the cubic 3C-modification. It is shown that the plastic deformation and the structure reorientation of ZnS crystals both are due to the motion of partial dislocation. The mechanism of the structure transition has been considered which consists in the step-by-step reorientation of close-packed layers due to the motion of partial dislocations. The kinetics of the structure transition has been investigated. It is shown that the number of stacking faults proportionally decreases with the increasing of the deformation and is independent of their concentration in the starting crystals. A very close coincidence is observed between the results of computations of the structure transition kinetics and the experimental dependence.

It is shown that not only macrostructure of crystals but also the local symmetry of impurity centers is changed due to plastic deformation of ZnS crystals. Thus, during plastic deformation of ZnS:Mn hexagonal crystals the symmetry points group of Mn^{2+} centers changes from C_{3v} to T_d .

Introduction of dislocations to the ZnS crystals changes character of relaxation from Cr^+ to Cr^{2+} and Fe^{2+} -centers when UV irradiation was stopped. The remainder concentration of deep acceptor Fe^{2+} -centers and filled Cr^+ -centers are preserved and level of this preservation depends on quantity of introduction dislocations. Such is possible, if the groups of these centers are divided in space of crystals only. The electrons under electric fields of charge dislocations push away from surrounding volume. As a result, the hole Fe^{3+} -centers will be localized inside the Rid 's cylinders mainly, and the electronic Cr^+ -centers between them.

From these results the value of linear density the electric charge unmovable dislocations $q > 0.28 \text{ e/site}$ and the Rid 's radius $R_0 = 10^{-5} \text{ cm}$ in ZnS crystals have been estimated.

This image shows a single sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

E-MRS'98 SPRING MEETING



SYMPOSIUM D

Thin Films Epitaxial Growth and Nanostructures

Symposium Organizers

- | | |
|--------------------|--|
| E. KASPER | Inst. für Halbleitertechnik, Univ. Stuttgart, Stuttgart, Germany |
| K.L. WANG | University of California, Los Angeles, CA, USA |
| H. HASEGAWA | Interface Quantum Electronics, Hokkaido Univ., Sapporo, Japan |

SYMPOSIUM D

Tuesday, June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - Selfassembled Structures

Chairpersons: **E. Kasper**, Inst. für Halbleitertechnik, Univ. Stuttgart, Stuttgart, Germany

H. Hasegawa, Interface Quantum Electronics, Hokkaido Univ. Sapporo, Japan

- D-I.1** 9:00-9:40 - Invited - **SELF-ASSEMBLED SEMICONDUCTOR ISLANDS STUDIED BY GRAZING INCIDENCE X-RAY TECHNIQUES**, **T.H. Metzger**, I. Kegel, P. Fratzl, R. Paniago and J.S. Peisl, Sektion Physik, Ludwig-Maximilians-Universität, 80539 München, Germany
A large number of potential device applications for dislocation-free quantum dots have been proposed during the last years. Their shape and strain distribution is crucial for adequate performance. We have developed a novel method to study the interdependence of strain and shape in self-assembled islands. These so-called "iso-strain-scattering" experiments are performed in grazing incidence diffraction (GID) geometry [1]. We will demonstrate this new approach by showing its application to three different systems:
1) We have investigated relaxed single-crystalline Ge islands grown on Si (111) by grazing incidence small angle scattering (GISAXS) and GID. We find that the Ge islands are strain-free single crystals of pyramidal shape, incoherently connected to the Si substrate. 2) Next, we report on dislocation-free, coherent, "naked" InAs dots grown on GaAs (100). From GISAXS we determine the axial symmetry and the average radius of the dots. In GID geometry we perform a strain-scanning experiment to investigate shape and strain of the islands: we tune in to a certain relaxation and study the small angle diffraction pattern near a large angle surface Bragg-peak. 3) Finally, the most complex system of Ge dot multilayers in Si (100) was studied by GID. We find highly correlated dots which form a square lattice in the plane of the sample surface. The most striking results on shape and strain of the dots are obtained from the analysis of the three dimensional reciprocal space maps. [1] I. Kegel et al, submitted to Phys. Rev. Lett.
- D-I.2** 9:40-10:00 **SELF-AGGREGATION OF InAs QUANTUM DOTS ON (N11) GaAs SUBSTRATES**, **S.Sanguinetti**, S.C.Fortina, S.Castiglioni, A.Miotto, E.Grilli, M.Guzzi, M.Henini*, A.Polimeni* and L.Eaves*, I.N.F.M. and Dip.to di Scienza dei Materiali dell'Università degli Studi, 20126 Milano, Italy,*Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, UK
We have obtained InAs quantum dots formation on a wide range of substrate orientations with different coverages. We show that the range of GaAs substrate orientations capable of dot self-aggregation is quite wide and that substrate orientation heavily affects ground state electronic properties. We report the low temperature photoluminescence characterisation of quantum dots grown on GaAs with InAs deposition on eight surfaces intermediate between (100) and (111), namely (N11)A/B GaAs substrates, where N ranges from 2 to 5, and a (100) sample chosen for comparison purposes. For each substrate orientation, three amounts of InAs were deposited. At 2K, all the samples show photoluminescence of evident quantum dot origin with an efficiency comparable to that of samples grown on (100) GaAs substrates. Photoluminescence spectra show inhomogeneously broadened, structured peaks in the 1.1 eV to 1.4 eV range. The quantum dots grown at low InAs coverages deserve a special interest both because of their photoluminescence efficiency and because of their narrow (25-30 meV) emission linewidth.
- 10:00-10:30 **BREAK**
- D-I.3** 10:30-10:50 **STM STUDY OF InAs QUANTUM DOTS BURIED IN GaAs**, **B. Legrand**, B.Grandidier, J.P.Nys, **D. Stiévenard**, Institut d'Electronique et de Microélectronique du Nord, IEMN, UMR9929, Département ISEN, 41 Bd Vauban, 59046 Lille Cedex, France, J.M. Gérard and V.Thierry-Mieg, Groupement Scientifique CNET-CNRS, 196 av. H.Ravera, 92220 Bagneux, France
InAs quantum dots buried in GaAs are studied using cross-sectionnal scanning tunneling microscopy in both imaging and spectroscopic modes on (110) cleaved surfaces *in vacuo*. The samples, grown using molecular beam epitaxy, contain series of 12 or 15 arrays of quantum dots. The images (300nm x 300nm) reveal the self-alignment of the dots. From images at atomic resolution (16nm x 16nm) combined with images taken at two opposite polarities (dual mode), we are able to analyze the nature of the atoms (arsenic, gallium and indium) as to the roughness of the dots interfaces along the [110] direction with the under- and overgrown GaAs layers. We show that the roughness of the upper interface is greater than the one of the lower interface. The difference (4.9 Å versus 3.7 Å) is explained by In segregation during the GaAs overgrowth. Moreover, we determine the strain distribution across one dot along the [001] growth direction. We evidence a compression of the GaAs at the edges of the dot and an expansion (up to ~ 7%) of the InAs with a partial elastic relaxation at the dot center, in agreement with a biaxial strain at the dot interfaces. Finally, local spectroscopic measurements on the dots allow the determination of the associated gap (1.25 eV), showing the electronic confinement in the dots.

D-I.4 10:50-11:10

SELF-ASSEMBLED NANOSTRUCTURES FROM π -CONJUGATED POLYMERS AT SURFACES, P. Samori and J.P. Rabe, Department of Physics, Humboldt University Berlin, Invalidenstr. 110, 10115 Berlin, Germany; V. Francke and K. Muelen, MPI for Polymer Research, Ackermann 10, 55021 Mainz, Germany

Making use of interfacial and intermolecular forces it is possible to build highly-oriented molecular assemblies. Macromolecular nanoribbons have been self-assembled on a non-conductive ultraflat substrate from solutions of an end-functionalized π -conjugated polymer, poly(para-phenyleneethynylene). They were visualized with dynamic Scanning Force Microscopy, revealing molecular cross-sections with a thickness of typically two molecular layers and a width distribution, which is described well by the distribution of molecular weights. These data indicate that the molecules are oriented with the conjugated backbone perpendicular to the long ribbon axis and the conjugated system parallel to the substrate. With thiol end-functionalization these ribbons are good candidates for molecular nanowires in a molecular scale electronic device. On the other hand, molecular resolution imaging with Scanning Tunneling Microscopy of both the polymer and its short oligomers enabled us to characterize the structure and dynamics of these molecules in a monolayer at the interface between a solution and the basal plane of graphite. We find a nematic order and a fractionation of the rod lengths around the peak of the molecular weight distribution.

D-I.5 11:10-11:30

SELF ORGANIZED VICINAL SEMICONDUCTORS SURFACES: A TEMPLATE FOR THE GROWTH OF NANOSTRUCTURES, D. Martrou, N. Magnea, CEA Grenoble DRFMC/SP2M, 17 Avenue des Martyrs, 38054 Grenoble Cedex, France

Self organized surfaces can be used as a template to create epitaxial nanostructures such as quantum wires and boxes. This technique based on the preferential growth at atomic step edges is compatible with the molecular beam epitaxy and can provide defects free structures contrary to processes based on nanolithography and ion etching. Furthermore it is not plagued by the technical difficulty and the very low yield of atomic manipulations using scanning probe microscopies. We demonstrate how the vicinal surfaces of semiconductors can form such a template when they self organize in a staircase or in a checkerboard array after molecular beam epitaxy.

The experiments are done on epitaxial CdTe (001) vicinal surfaces studied by scanning tunneling microscopy. We take advantage of the particular growth mode of CdTe where the 2-D growth proceeds by the flow of (100) steps and not (110) as in Si or GaAs. The main consequence is the absence of any anisotropy in the equilibrium shape of 2-D islands. Then when the epitaxy is performed on a surfaces with steps parallel to the (100) directions, we obtain a network of regularly spaced terraces in the form of a staircase. If the steps are at 45° from the (100) directions i.e. parallel to the (110) axis there is a definite set of growth conditions where the equilibrium configuration consists of square terraces ordered in a checkerboard array. The nodes of this superlattice whose parameter is only defined by the miscut angle, should act as nuclei for the ordered growth of nanostructures.

D-I.6 11:30-11:50

SURFACTANT INDUCED GIANT FACETING OF VICINAL Si(001), M. Horn von Hoegen, Institut für Festkörperphysik, Universität Hannover, Appelstr. 2, 30167 Hannover, Germany

Adsorbate induced faceting and step arrangement control of vicinal single crystal semiconductor surfaces are key techniques in the self-organized formation of 1-dimensional nano structures. Utilizing selective deposition techniques growth of nano wires will be possible by decoration. Crucial for the success are key parameters as the width, length and height of ordered step bunches, the straightness of the step edges, and the regularity of the arrangement of atomic steps or stepbunches.

Here we demonstrate that monolayer adsorption of Au on vicinal Si(001) at elevated temperature results in the formation of extremely straight and elongated (001)-superterraces with a length in the nm range and an average separation up to 1000 nm. Conservation of macroscopic misorientation requires extremely elongated (119)-facets separating then (001)-terraces and with an aspect ratio of more than 1:10000. These structures may now be used as template for selective deposition of nano wires.

The dramatic large scale morphological transformation of a flat surface into a hill-and-valley structure could be observed even with the bare eye. The parallel arrangement of superterraces acts as an irregular optical phase grid: Illumination with white light results in stripes of all possible diffraction colours.

D-I.7 11:50-12:10

NANOSCALE SELECTIVE AREA GROWTH OF ZnSe/ZnS DOTS ON (001) GaAs COVERED WITH CARBONACEOUS MASKS PATTERNED BY AFM, A. Avramescu, A. Ueta, K. Uesugi, I. Suemune, Res. Inst. Elect. Sci, Hokkaido University, Sapporo 060, Japan, H. Machida and N. Shimoyama, Trichemical Laboratory, Uenohara 8154-217, Yamanishi 409-01, Japan

Selective-area growth is a forward technique for growth of different semiconductor structures and is continuously advancing toward the nanoscale range. II-VI compound semiconductors have potentials for low-temperature selective-area growth, which is a feature necessary for optoelectronic integration. In this paper, ZnS and ZnSe dot structures were selectively grown using carbonaceous masks patterned with an Atomic Force Microscope (AFM) with the resolution well below 100 nm. The carbonaceous film was deposited on (001) GaAs substrate by near-surface decomposition of the residual oil molecules in a Scanning Electron Microscope and its thickness was controlled to 2-3 nm by the exposure dose. The mask for the selective growth was patterned by anodization through a conductive cantilever in the AFM. The anodized carbonaceous film is removed up to the GaAs surface by etching in HCl. ZnSe/ZnS dot structures were grown on the patterned substrates by MOCVD. The growth was done at low substrate temperatures in the range of 300 to 400°C. Diethyl zinc, diisobutyl selenide and diisobutyl sulfide were used as precursors. Luminescence around 400 nm was observed from these dot structures.

12:10-14:10

LUNCH

Tuesday, June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-midi

SESSION II - Novel Growth Methods

Chairpersons: H. Hasegawa, Interface Quantum Electronics, Hokkaido Univ. Sapporo, Japan
K. Eberl, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

D-II.1 14:10-14:30

FORMATION OF HIGHLY UNIFORM InGaAs RIDGE QUANTUM WIRES BY SELECTIVE MBE GROWTH ON NOVEL InP PATTERNED SUBSTRATES, H. Fujikura and H. Hasegawa, Research Center for Interface Quantum Electronics and Graduate School of Electronics and Information Engineering, Hokkaido University, Sapporo 060-8628, Japan

Recently, we have successfully grown high quality and narrow (30nm) InGaAs quantum wire (QWR) arrays by selective MBE growth on patterned InP substrates having <-110>-oriented mesa-strips. Coulomb oscillations have also been demonstrated in single electron transistors formed putting wrap gates on such QWRs. For such electronic applications, the uniformity of the starting QWRs is vitally important.

The purpose of this paper is to identify various factors related to wire non-uniformity and to improve the uniformity by modifications of epitaxial growth methods. Main results are the following:

1) Among various factors causing the inhomogeneity of the wire, the most dominant one has been found to be irregular waving of the top of the (311)A/(111)A InAlAs ridge grown on the InP mesa-strips before QWR growth. This waving is due to appearance of extra (110) facets on the (111)A sidewalls in a random fashion. CL emission from such inhomogeneous wires was discontinuous and broken along the wire direction.

2) By using mesa-strips having directions slightly mis-orientated from the exact <-110> direction, the extra (110) facets were aligned systematically with regular short periods, resulting in drastic suppression of the waving of the ridge top and in improvement of the wire uniformity.

3) Alternatively, by using <-110>-oriented mesa-strips whose width was intentionally changed along the mesa periodically, the extra facets were found to gather at boundaries between the wide and the narrow width regions, leading to complete removal of the extra facets and the waving of ridge from the wide width region having a length of several μm .

D-II.2 14:30-14:50

RETARDED DIFFUSION OF BORON IN Si DUE TO THE FORMATION OF AN EPITAXIAL CoSi_2 LAYER, L. Kappius, H. L. Bay, S. Mantl, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, 52425 Jülich, Germany, A. K. Tyagi, U. Breuer, Zentralabteilung für Chemische Analysen, Forschungszentrum Jülich, 52425 Jülich, Germany

Secondary ion mass spectrometry (SIMS) investigations revealed that during oxidation of thin CoSi_2 -layers the diffusion of B in the underlying Si is strongly retarded. Thin cobaltdisilicide layers (20 nm) grown by molecular beam allotaxy (MBA) on Si(100) substrates can be patterned by local oxidation. This process provides minimum gaps as small as 60 nm between silicide pads by conventional lithography. For electrical applications of this process it is important to investigate its influence on the dopant diffusion. In the present study B doping superlattices (DSLs) consisting of six B spikes with peak concentrations of 10^{16}cm^{-3} and peak centres spaced 100 nm apart were grown by MBE. The shallowest spike was capped with 100 nm Si followed by 20 nm of CoSi_2 . Similar DSL specimens were also grown without a silicide cap layer. The specimens were oxidized at temperatures ranging from 800°C to 1100°C for various times. B concentration depth profiles were measured by SIMS. For specimens without CoSi_2 layer we observed oxidation enhanced diffusion of B in Si in accordance with the literature. However, B diffusion in silicide capped specimens was found to be retarded by about a factor of 20 as compared to specimens without silicide layer. The measured diffusivity was even less than the intrinsic diffusivity of B in Si.

D-II.3 14:50-15:10

SURFACTANT MEDIATED EPITAXY OF Ge ON Si: PROGRESS IN GROWTH AND ELECTRICAL CHARACTERIZATION, M. Kammler, D. Reinking, K. R. Hofmann, Institut für Halbleitertechnologie, Applestr. 11, M. Horn von Hoegen, Institut für Festkörperphysik, Appelstr. 2, Universität Hannover, 30167 Hannover, Germany

The deliberate use of an adsorbed monolayer of a group V element as surfactant (here Sb and Bi) during Ge/Si epitaxy hinders islanding and allows to grow smooth and continuous epitaxial Ge films on Si and Si films on top of the Ge films. The 4.2% lattice mismatch between Si and Ge is accommodated by a quasiperiodic array of dislocations which are confined to the Si-Ge interfaces. This allows to grow strain relieved, relaxed Ge and Si films of arbitrary thickness, which are almost free of defects. Electron Hall mobilities of more than 3000 cm^2/Vs at RT are routinely obtained (11000 cm^2/Vs at 77K) for 1000 nm thick relaxed Ge films. Both values belong to the best ever reported for Ge films grown on Si. The carrier density of $1 \times 10^{16}\text{cm}^{-3}$ is determined by Hall measurements. Germanium p-n diodes have been successfully fabricated and first electrical characterizations indicate that the film quality is suitable for device fabrication.

In this contribution we also present first results on successfully grown relaxed Si layers on Ge(111) films, the relaxation mechanism and its epitaxial quality.

SYMPOSIUM D

D-II.4 15:10-15:30

GROWTH AND OPTICAL PROPERTIES OF DIRECT ENERGY GAP $\text{Sn}_x\text{Ge}_{1-x}$ ALLOYS ON Ge (001) AND Si (001), R. Ragan, G. He, H.A. Atwater, T.J. Watson
Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA 91125, USA

We report infrared transmission measurements indicating a tunable direct energy gap in pseudomorphic epitaxial $\text{Sn}_x\text{Ge}_{1-x}$ /Ge (001) and strain-relieved $\text{Sn}_x\text{Ge}_{1-x}$ /Si (001) substrates. Absorption measurements for $\text{Sn}_x\text{Ge}_{1-x}$ /Si (001) were derived from thickness-dependent transmission data. These alloys exhibited a decrease in direct energy bandgap from 0.8 eV to 0.25 eV as Sn concentration was varied from $0 < x < 0.15$. More recently, similar data have been obtained for high-quality, pseudomorphic single-layer $\text{Sn}_x\text{Ge}_{1-x}$ /Ge (001) alloy films for $0 < x < 0.115$ that were characterized by X-ray reflectivity measurements, Rutherford backscattering, and transmission electron microscopy. Films were found to be fully pseudomorphic, compositionally uniform with the absence of Sn segregation, and dislocation free for single layers up to 100 nm thick. Superlattices with periods as short as 25 nm and alloy layers as thin as 5 nm exhibited abrupt interfaces. Low temperature ($T = 180^\circ\text{C}$) fabrication of $\text{Sn}_x\text{Ge}_{1-x}$ alloys by molecular beam epitaxy and the existence of a tunable direct energy bandgap in the near to mid-infrared may enable monolithic integration of $\text{Sn}_x\text{Ge}_{1-x}$ photoconductive or photovoltaic infrared devices on fully-processed Si integrated circuits.

15:30-16:00

BREAK

SESSION III - Poster Session I - Selfassembly and Strain Adjustment

16:00-18:00

See programme of this poster session p. D-15 to D-19.

Wednesday, June 17, 1998
 Mercredi 17 juin 1998

Afternoon
 Après-midi

SESSION IV - Electronic Devices

Chairpersons: M. Kelly, University of Surrey, Guildford, UK
 K. De Meyer, IMEC, Leuven, Belgium

- D-IV.1** 14:10-14:50 - Invited - **SILICON QUANTUM INTEGRATED CIRCUITS (SiQUIC), D.J. Paul**, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, UK; G. Redmond, B.J. O'Neill and G. Crean, NMRC, Lee Maltings, Prospect Row, Cork, Ireland; S. Mantl, ISI Forschungszentrum Jülich, 52425 Jülich, Germany; I. Zozoulenko and K.F. Berggren, University of Linköping, Linköping 58183, Sweden; J.-L. Lazzari, F. Arnaud d'Avitaya and J. Derrien, CRMC2-CNRS, Campus de Luminy, 13288 Marseille Cedex 9, France
- Silicon Quantum Integrated Circuits is a Esprit MEL-ARI project (No. 22987) with the object of demonstrating Si/SiGe quantum devices produced on a CMOS production line. Initially heterostructure FETs are being produced to allow CMOS compatible processes to be characterised while later resonant tunnelling diodes (RTDs) and velocity modulation transistors (VMTs) will be demonstrated. This paper will report on the initial results of producing a heterostructure FET on a CMOS line including material quality and defects, etching, implantation, gate oxides, thermal budgets and passivation. Theoretical predictions of expected performance from the RTDs and VMTs will also be presented along with potential applications.
- D-IV.2** 14:50-15:10 **STRUCTURAL, ELECTRICAL AND HF CHARACTERIZATION OF HIGH SPEED GRADING AND STEP BASE Si/SiGe HBT'S, J. Weller**, H. Jorke, K. Strohm, J.-F. Luy, H. Kibbel, H.-J. Herzog, Daimler-Benz Research Center Ulm, Wilhelm-Runge-Str.11, 89081 Ulm, Germany; R. Sauer, Universität Ulm, Albert-Einstein-Allee 45, 89081 Ulm, Germany
- In heterojunction bipolar transistors (HBT) cutoff frequencies are limited by time constants of electron transport across the base and the collector space charge region. This favours use of small base widths. This however increases base resistance which leads to a decrease in the maximum frequency of oscillation. A way out of this trade-off is to accelerate the minority-carrier transport by grading the alloy composition in the SiGe base which leads to a fast drift transport. Another approach to shorten the base transit time was suggested by Luryi et al. who considered a step base concept. Beside their potential to accelerate carrier transport a graded or stepped base transistor may show an active transistor behavior above the cutoff frequency. This is expected to occur at a phase shift of π due to the finite transit time across the base. This could enable the development of new high speed transistors. This work presents first results on those structures in the material system Si/SiGe regarding structural properties, electrical characteristics as well as high frequency behaviour.
- D-IV.3** 15:10-15:30 **CARRIER MOBILITIES IN MODULATION DOPED $\text{Si}_{1-x}\text{Ge}_x$ HETEROSTRUCTURES WITH RESPECT TO FET APPLICATIONS, G. Höck**, Dept. of Electron Devices and Circuits, University of Ulm, Albert-Einstein-Allee 45, 89081 Ulm, Germany; M. Glück, T. Hackbarth, H.-J. Herzog, Daimler-Benz AG, Wilhelm-Runge-Str. 11, 89081 Ulm, Germany
- Carrier mobilities in both p- and n-type modulation doped SiGe heterostructures were investigated by magnetic field dependent Hall (B-Hall) technique. B-Hall allows a selective determination of mobility and sheet carrier density in the channel and in parasitic parallel conducting layers.
- The heterostructures were grown by MBE, consisting of a strained $\text{Si}_{1-x}\text{Ge}_x$ channel on a $\text{Si}_{1-y}\text{Ge}_y$ strain relieved buffer (SRB) with $x-y = 0.3$. Structural assessment was done by X-ray diffraction and crosssectional TEM. We have investigated the channel mobility of p-type devices as a function of Ge content x in the channel. As a result we found, that the room temperature hole mobility in the channel increases from 635 cm^2/Vs for $x = 0.67$ up to 1665 cm^2/Vs for a pure Ge channel, which is close to the value of undoped bulk Ge. In case of a n-type Si channel on a $\text{Si}_{0.7}\text{Ge}_{0.3}$ SRB, a room temperature electron mobility of 2700 cm^2/Vs was measured.
- 15:30-16:00 **BREAK**
- D-IV.4** 16:00-16:40 - Invited - **ARCHITECTURES FOR NANOSTRUCTURE DEVICES, V. Roychowdhury**, University of California, Los Angeles, CA 90095-1594, USA
- We shall review some of the recent proposals for circuit and computational concepts in nano-electronics. In particular, two classes of computing models will be discussed. The first class is based on semi-classical global models (e.g., Coulomb blockade, and single electronics), where the circuit functions are realized through cooperative, nonlinear interactions between coupled quantum dots. We show that these circuits can realize a broad spectrum of functions ranging from global cooperative computations such as solutions of combinatorial optimization problems at one end, to relatively simple computations such as implementations of logic functions at the other. The second class of circuits to be addressed in the talk, is based on the presence of discrete energy levels in nanostructure devices (e.g., those found in quantum dots), and the ability to generate mixed states using π -pulses. In particular, we shall present computing units based on optically coupled arrays of quantum dots that can perform both classical Boolean operations and can realize the basic building blocks or quantum computation. We shall also present a brief overview of recent experimental efforts towards realizing basic units of the computational models introduced in the talk.
- ** This talk is primarily based on joint work with Dr. Kang Wang at UCLA, Dr. Dave Janes and S. Dutta at Purdue Univ., and Dr. S. Bandyopadhyay at Univ. of Nebraska-Lincoln**

SYMPOSIUM D

D-IV.5 16:40-17:00

SIMULATION OF A NON-INVASIVE CHARGE DETECTOR FOR QUANTUM CELLULAR AUTOMATA, M. Macucci, C. Ungarelli, G. Iannaccone, M. Governale, Dipartimento di Ingegneria dell'Informazione, Università di Pisa, Via Diotisalvi 2, 56126 Pisa, Italy

Logic circuits based on the Quantum Cellular Automata (QCA) paradigm offer an interesting alternative to traditional architectures used for computation. The basic building block of a QCA system is a cell made up of four or five quantum dots, and containing two electrons, which can align along one of the two diagonals, giving rise to two possible polarization states. It has been shown that cell polarization can propagate along a chain of cells and that properly assembled two-dimensional arrays of cells allow the implementation of logic functions. The results of any computation performed with such arrays consist in the polarization state of some output cells. This information must be read without perturbing it, therefore a non-invasive charge probe is needed. We have performed a three-dimensional Poisson-Schroedinger self-consistent simulation of a system made up of a quantum dot and a nearby quantum point contact defined by means of depleting metal gates in a two-dimensional electron gas at a GaAs/AlGaAs heterointerface. We have computed the number of electrons in the dot as a function of the bias voltages applied to the gates, and the resulting variations in the quantum point contact resistance. Our results indicate that even the extremely small variations of the confinement potential due to the addition or removal of a single electron produce measurable variations of the resistance, as shown in recent experiments. The results obtained for different gate layouts are compared, and design criteria are derived for achieving optimal sensitivity.

SESSION V - Poster Session II - Growth

17:00-18:30

See programme of this poster session p. D-20 to D-26.

Thursday, June 18, 1998
Jeudi 18 juin 1998

Morning
Matin

SESSION VI - Island and Wire Formation

Chairpersons: G. Abstreiter, Walter Schottky Institut, Garching, Germany
M. Lagally, University of Wisconsin-Madison, Madison, WI, USA

D-VI.1 9:00-9:20

NUCLEATION AND GROWTH OF SELF-ASSEMBLED Ge/Si(001) QUANTUM DOTS BY UHV-CVD, V. Le Thanh, P. Boucaud, D. Débarre, C. Ulysse, D. Bouchier, and J.-M. Lourtioz, Institut d'Electronique Fondamentale, Université Paris-Sud, 91405 Orsay, France

During the past few years, a considerable amount of work has been devoted to the formation of quantum dots (QD's) due to their potential interest for electronic and optoelectronic device applications. Among the different ways to produce QD's, special attention has been paid to the self-assembled technique which takes advantage of the transition from two-(2D) to three-dimensional (3D) growth mode occurring during growth in a highly lattice-mismatched heteroepitaxial system. To concretize the application potential, it is essential to control the size and the size distribution of QD's. This demands a detailed understanding of the microscopic processes involved in thin film growth, in particular near the 2D-3D transition.

In this work, we present results on the kinetics of Ge/Si(100) islanding growth by UHV-CVD. The island formation was studied using in-situ reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and photoluminescence spectroscopy (PL). We evidence the existence of an intermediate phase between 2D layers and macroscopic 3D islands, its appearance is observed well before the RHEED 2D-3D transition. This phase consists of small islands exhibiting {501} facets; their average dimensions are ~ 40nm in length and ~ 1 nm in height. The main difference between these islands and the 'hut' clusters observed by MBE is that they all have square bases and a very low concentration (~ 6.10¹⁰cm⁻²). We demonstrate that these islands are metastable and they act as a precursor for the formation of 3D macroscopic islands. Furthermore, we show that the surface mobility of Ge adatoms is the key parameter which determines the evolution of 3D islands. Two regimes of mobility are clearly identified: in the high mobility regime, the islands have very broad size distributions, while in the low mobility regime, islands with remarkably low size dispersion (< 3%) are formed.

D-VI.2 9:20-9:40

PHOTOLUMINESCENCE OF Ge DOTS GROWN BY ULTRA - HIGH- VACUUM CHEMICAL VAPOR DEPOSITION ON Si(001), P. Boucaud, V. Le Thanh, D. Débarre, D. Bouchier, J.-M. Lourtioz, IEF, Université Paris XI, 91405 Orsay, France

Quantum dots made of semiconductor heterostructures are entering the field of nanoelectronics. These artificial atoms can be grown on a silicon substrate using a self-assembled growth method of germanium dots. The key feature for these Ge dots is to control their size and distribution. In this work, we will present the growth monitoring of Ge dots by photoluminescence. The islands are grown at different temperatures (700°C or 550°C) by ultra-high-vacuum chemical vapor deposition. Four distinct stages of the growth are clearly evidenced by photoluminescence as a function of growth time: the formation of a 2-D wetting layer, the nucleation of small islands (1nm height, ~40 nm base length) before the onset of the 2D-3D growth transition evidenced by RHEED, the coarsening of the islands and the onset of new photoluminescence lines after the coalescence of the clusters. The photoluminescence observed after coalescence consists of a no-phonon and phonon assisted recombination transitions. The average size and the distribution homogeneity of the dots are found to be dependent on the growth temperature. The broadening of the photoluminescence of the small clusters (~100 meV) is larger than the broadening of the large clusters (~40 meV). The temperature dependence of the photoluminescence varies with the dot size, as expected from thermionic emission. The photoluminescence results will be correlated to the structural characterization of the layers.

D-VI.3 9:40-10:00

MORPHOLOGY AND PHOTOLUMINESCENCE OF Ge ISLANDS GROWN ON Si (001), M. Goryll, L. Vescan and H. Lüth, Institute of Thin Film and Ion Technology, Research Centre Jülich, 54245 Jülich, Germany

The use of self-organization of nanostructures during growth of materials having a high lattice mismatch e.g. Ge on Si offers new possibilities for device applications. We present a study on the temperature dependence of the Ge island morphology determined by atomic force microscopy (AFM). The Ge layers were grown on Si(001) substrates by low pressure chemical vapour deposition. Island size statistics derived from the atomic force micrographs show a trimodal size distribution at high growth temperatures and high average Ge layer thicknesses, whereas at high temperatures and low Ge layer thicknesses only a narrow monomodal island size distribution exists. Low growth temperatures of the Ge layer offer the possibility of fabricating kinetically limited islands of small size. Transmission electron micrographs reveal the type of relaxation of the Ge islands and the shape of islands after being capped by a Si overlayer. A correspondence between the broadening of the spectral emission and the island morphology can be concluded from photoluminescence measurements. Multiple stacked island layers exhibit a significant increase of integral intensity in comparison with a single layer of islands, grown under equal conditions. A clear vertical correlation between island positions in different layers and a continuous enlargement of island size in upper layers is found on transmission electron micrographs of stacked island layers.

10:00-10:30

BREAK

SYMPOSIUM D

D-VI.4 10:30-10:50

C-INDUCED Ge DOTS: A VERSATILE TOOL TO FABRICATE ULTRA-SMALL Ge NANOSTRUCTURES, O.G. Schmidt, S. Schieker, K. Eberl, Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany and O. Kienzle, F. Ernst, Max-Planck-Institut für Metallforschung, Seestrasse 92, 70174 Stuttgart, Germany

Pre-growth of a small amount of C on Si induces ultra-small, only 10 to 15 nm wide and 1 to 2 nm high, Ge quantum dots, although the critical thickness d_c for planar Ge growth is not exceeded. These CGe dots exhibit an anisotropic strain field which in vertical direction extends into the Si far beyond their actual height. Like for conventionally grown Ge islands, the anisotropic strain fields are capable to induce vertically aligned Ge dots. We present a coherent quantum dot stack, consisting of an initial 0.2 ML C/ 3 ML Ge dot layer, followed by 5 layers of 4 ML Ge. Each layer is separated by 2 nm Si. The islanding process is again initiated before d_c for planar Ge growth is reached and results in only 20 nm wide and 2 nm high vertically correlated Ge dots. However, if we substitute the pure Ge layers by a stack of CGe dots, no vertical correlation is observed. We explain this phenomenon by the kinetically limited process of CGe island formation, itself. Photoluminescence experiments show a strong energy red-shift for closely stacked CGe dots.

D-VI.5 10:50-11:10

LATERAL ORDERING OF SELF-ASSEMBLED Ge ISLANDS, Jian-hong Zhu, K. Brunner, G. Abstreiter, Walter Schottky Institut, Technische Universität München, Am Coulombwall, 85748 Garching, Germany

Two-dimensionally ordered arrays of self-assembled Ge islands are fabricated by deposition of several monolayers of Ge on vicinal Si(001) surfaces with regular ripples at about $T_s=500^\circ\text{C}$ in a molecular beam epitaxy system. Due to the instability of the SiGe vicinal surfaces under stress against step-bunching and a vertical correlation of the rippled interfaces, deposition of a 2.5 nm $\text{Si}_{0.55}\text{Ge}_{0.45}/10$ nm Si multilayer results in regular ripples on vicinal surfaces with a typical period of 100 nm. The ripples lead to a long-range line-up of the Ge islands along their directions, while the strong repulsive interaction between the dense Ge islands determines their relative arrangement on different step bunches of a ripple. The ordering pattern of the Ge islands can be tuned by the ripple direction and the coverage of the Ge deposited. The Ge islands show a compact shape with a square-like base and have a narrow size distribution due to the ordering and the limitation of their base diameter by the step bunch width. In contrast, when deposited directly on well-prepared vicinal Si(001) surfaces with biatomic steps, the Ge islands are only partly aligned along the step direction, although they have a compact {105} faceted pyramid-like structure [1]. No ordering of Ge islands has been observed, however, when a flat Si(001) surface or a Si(118) surface, which can be regarded as a vicinal Si(001) surface with a large mis-cut angle of 10° , is employed, where no obvious step-bunching occurs.

[1] Jian-hong Zhu et al. Appl. Phys. Lett. 72, 424 (1998).

D-VI.6 11:10-11:30

SELF ORGANISATION OF Ge DOTS ONTO Si SUBSTRATES : INFLUENCE OF THE MISORIENTATION, M. Abdellah, I. Berbezier, CRMC2 - CNRS Campus de Luminy, Case 913, 13288 Marseille France, P. Dawson, UMIST, PO Box 88, Manchester M60 1QD, UK, M. Serpentine, G. Brémont, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 Av. A. Einstein, 69621 Villeurbanne Cedex, France, B. Joyce, IRC, Imperial College of Science, Technology and Medicine, The Blackett Laboratory, Prince Consort Road, London SW7 2BZ, UK

Gas Source Molecular Beam Epitaxy (GSMBE) of self organised germanium dots on Si substrates has been investigated. The driving idea was to take benefit of the periodic surface undulation that occurs in highly lattice mismatched systems, as SiGe/Si, to locally (indeed, at the top of these undulations) initiate the nucleation of an array of small size 3D islands. Exploiting our previous results which showed that the period of the undulations of SiGe layers was decreasing when the misorientation of the Si substrate increased, we have successively deposited by GSMBE, at 550°C (using germane and disilane as precursor gases) a 100 Å thick $\text{Si}_{0.3}\text{Ge}_{0.7}$ layer and various amounts of pure Ge on 10° off (indeed (118) oriented surfaces) Si (100) substrates. Using Transmission Electron Microscopy (TEM) we have found that, as expected, and according to Stranski-Krastanow model, 3D Ge islands, with no significant creation of interfacial misfit dislocation, were formed at the top of the undulations once a certain critical thickness was reached. This critical thickness has been found to depend on the misorientation and was estimated to 7 and 4 monolayers for the 10° off and the nominal (100) substrates respectively.

D-VI.7 11:30-11:50

PERFECT BISMUTH LINES IN SILICON EPILAYER, K. Miki, K. Sakamoto, Electrotechnical Laboratory, Tsukuba 305-8568, Japan; D.R. Bowler, J.H.G. Owen, G.A.D. Briggs, Materials Dept., Oxford University, Parks Road, Oxford OX1 3PH, UK

Atomically perfect bismuth line forms on Si(001) by a selective desorption process around the temperature at which most of the bismuth desorbs (790 - 870 K) from bismuth epitaxial layers. The lines are perpendicular to the silicon dimer rows; they are 1 nm wide and can be hundreds of nm long in a flat Si(001) surface. They are utterly free of kinks or other defects. In our proposed model three silicon dimers in the surface are replaced with two dimers, with a rebonded missing dimer defect between them. We propose a knock-on effect model to explain the mechanism by which the line extends: the line is terminated by silicon dimer vacancies and bismuth dimers diffuse into the vacancy sites.

The perfect Bi lines can be buried in Si epitaxial layer by subsequent growth. They are very stable against the growth and require higher energy for their surface segregation than well-known (2x1): Bi surface which has been demonstrated to be a very useful surfactant [1]. The remained Bi density was $9 \times 10^{13}/\text{cm}^2$ at the growth temperature of 400°C . It means that most of the Bi line survived against the over growth.

[1] Kunihiro Sakamoto, Hirofumi Matsuhata, Ken'ichi Kyoya, Kazushi Miki, and Tsunenori Sakamoto: Jpn. J. Appl. Phys. 32, L204 (1993).

11:50-14:10

LUNCH

Thursday, June 18, 1998
Jeudi 18 Juin 1998

Afternoon
Après-midi

SESSION VII - Analysis and Modelling of Nanostructures

Chairpersons: J. Derrien, CRMC2-CNRS, Marseille, France

K. Eberl, Max-Planck-Institut für Festkörpersphysik, Stuttgart, Germany

- D-VII.1** 14:10-14:50 - Invited - **IN-SITU LEEM OBSERVATION OF ISLAND GROWTH, P. Sutter**, University of Wisconsin-Madison, WI 53706, USA
In heteroepitaxial systems such as $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(100)$, the initial relaxation of misfit strain involves the formation of coherent, faceted three-dimensional (3D) islands with nanometer dimensions. Proper choice of growth parameters, utilizing thermodynamic and kinetic constraints, may induce such islands to assume identical size and shape and to organize into a regular array, as required for application in future devices. In-situ microscopy techniques, which allow for dynamic imaging of individual 3D islands in the presence of a growth flux and in interaction with other clusters in an array, are uniquely suited for studying the fundamental mechanisms of nucleation, growth and ripening of such ensembles. This talk reviews recent in-situ microscopy techniques and their specific contrast mechanisms, which can be used to characterize the geometry of 3D islands in real time. Open questions regarding the initial formation of islands and their interaction to form ordered arrays are outlined and are discussed on the basis of observations by low-energy electron microscopy (LEEM).
- D-VII.2** 14:50-15:10 **X-RAY DIFFRACTION ANALYSIS OF STRAIN RELAXATION IN FREE STANDING AND BURIED LATERALLY PATTERNED SQW STRUCTURES, N. Darowski**, U. Pietsch, Department of Physics, University of Potsdam, Germany, S. Kycia, Q. Shen CHESSE, Cornell University, Ithaca N.Y., USA
Lateral wire nanostructures defined on a MBE grown GaAs/GaInAs/GaAs SQW have been investigated before and after overgrowth with (Al)GaAs. The geometric parameters were defined by electron beam exposure subsequent wet-chemical (triangular shaped) or ion beam etching (rectangular). Some of the samples were overgrown by a second MBE step. The strain analysis was performed by high resolution X-ray diffraction (HRXRD) and depth resolved X-ray grazing incidence diffraction (GID). In first case we determined the average out-of plane and in-plane strain acting in the nanostructure. Whereas the in-plane strain appears tensile at the free standing wires we found compressive strain after overgrowth. GID experiments enabled us to determine the wire shape and their strain profile separately. For the overgrown samples we found a lateral strain modulation within the top layer appearing up to the completely smooth sample surface, induced by the buried nanostructure itself. The evaluated strain parameter depend on the wire shape and can be compared with finite element calculations and used to interpret respective photoluminescence experiments.
- D-VII.3** 15:10-15:30 **STUDY OF DEFECTS FORMATION IN GaSb/(001)GaAs ISLANDS BY MONTE CARLO SIMULATION, J. Dalla Torre***,**, M. Djafari Rouhani*,**, R. Malek*, *Laboratoire d'Analyse et d'Architecture des Systèmes, 7, Av. du Colonel Roche, 31077 Toulouse Cedex, France, **Laboratoire de Physique des Solides, Université Paul Sabatier, 31062 Toulouse Cedex, France
The GaSb/(001)GaAs is a large lattice mismatch system (8%). Films thinner than 100Å are experimentally shown to be constituted of isolated islands, and most of them contain at least one stacking fault. The aim of this work is to investigate the mechanism of formation of these defects. Our simulation is based on a Monte Carlo algorithm. It is organized around elementary atomic processes. The strain is introduced through an elastic energy term based on a simplified Valence Force Field approximation and stress is relaxed along atomic chains at each of the 10 occurrences needed to perform a simulation. We will discuss the way to create stacking fault defects and we will examine the influence of the substrate morphology on their creation in GaSb islands.
- 15:30-16:00 **BREAK**
- D-VII.4** 16:00-16:20 **MODELLING OF INITIAL STAGE OF SILICON EPITAXY ON POROUS SILICON (111) SURFACE, L.N. Aleksandrov**, P.L. Novikov, A.V. Dvurechenskii, V.A. Zinovyev, Institute of Semiconductor Physics, Academy of Science, 630090 Novosibirsk, Russia
The atomic structure of Porous Silicon (PS) holds short and long order in spite of local that allows to use PS as a substrate for epitaxial deposition of crystal films. In the present paper the mechanism of initial stage of epitaxial deposition of Si on PS(111) surface is studied by computational modelling. Considering the adatom surface diffusion under MBE by Gilmer, we suppose two new possibilities: the vacancies and overhanging are admitted; the activation energy of diffusion depends upon the occupation of adatom environment, including all 12 positions in the second coordination sphere. The suggested and the classical models give the identical description of surface diffusion on smooth Si(111) surface. The simulation is designed on three-dimensional 160x160x20 mesh. The typical fragments of layer cross-section before, during and after Si deposition on PS are shown. The film growth kinetics and change in overgrown pore morphology on atomic scale were studied. The morphology of the film surface was characterized numerically by step density function. The statistical analysis of atomic bond configurations for adatoms inside pores allowed to specify the detailed mechanism of initial stage of Si epitaxy on PS.

SYMPOSIUM D

D-VII.5 16:20-16:40

EARLY STAGES OF GROWTH AND NANOSTRUCTURE OF $\text{Pb}(\text{Zr,Ti})\text{O}_3$ THIN FILMS OBSERVED BY ATOMIC FORCE MICROSCOPY, F. Craciun, P. Verardi, M. Dinescu*, F. Dinelli**, O. Kolosov**, CNR Istituto di Acustica, Area di Ricerca Roma-Tor Vergata, Rome, Italy, *Institute of Atomic Physics, Bucharest, Romania, **Department of Materials, University of Oxford, UK

Ferroelectric lead zirconate titanate (PZT) thin films were widely investigated for applications like piezoelectric microdevices, non-volatile memory elements, nonlinear optical devices, pyroelectric detectors etc. While performant films deposition has been obtained with many different techniques, relatively little knowledge regarding their initial growth stages and mechanisms has been achieved. We prepared PZT layers with different thicknesses on Au coated Si(100) and Si(111) wafers by pulsed laser deposition, using the same set of experimental conditions: a Nd-Yag laser, 1064 nm, 10 ns, 10 Hz, substrate temperature 370°C, oxygen pressure 150 mTorr, laser fluence 25 J/cm², by varying the number of laser pulses. Different analysis like XRD, EDS, XPS, SIMS put in evidence the crystallographic structure and chemical composition of films. Surface morphology was examined by atomic force microscopy (AFM). Analysis of films with very few atomic layers suggests that the growth proceeds by Volmer-Weber island-growth mechanism. Different geometrical, chemical and kinetic factors responsible for this type of growth are discussed. Comparative AFM analyses of surface roughness performed on films with different thickness allow to study the interface width evolution during the growth and to predict the conditions for obtaining films with smooth surface.

D-VII.6 16:40-17:00

DYNAMIC PROPERTIES OF TRIONS AND EXCITONS IN MODULATION-DOPED CdTe/CdMgTe QUANTUM WELLS, D. Brinkmann, J. Kudrna, E. Vanagas, P. Gilliot, and R. Lévy, Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe d'Optique Non Linéaire et d'Optoélectronique, UMR 46 CNRS-ULP-ECPPM, 23, rue du Loess, B.P. 20 CR, 67037 Strasbourg Cedex, France, A. Arnoult, J. Cibert, and S. Tatarenko, Laboratoire de Spectrométrie Physique, Université Joseph Fourier I - CNRS (UMR 55 88), B.P. 87, 38402 Saint Martin d'Hères Cedex, France

We report on the phase and population relaxation of neutral excitons (X) and positively charged excitons (X⁺), called trions, in modulation doped CdTe/CdMgZnTe multiple quantum wells. The coherent dephasing of both quasiparticles is investigated by means of transient four-wave mixing. Exciting with picosecond laser pulses we can separately determine the dephasing times T_2 of excitons and trions. We observe a relatively slow dephasing of trions in comparison with excitons. When both resonances are simultaneously excited by spectrally large femtosecond pulses, the photon echo traces show modulations due to quantum beats or polarisation interferences with a period determined by the energy splitting between the resonances. In addition, time-resolved photoluminescence experiments are carried out to study the population dynamics of excitons and trions. The time constants determining the population relaxation are found to be very similar for both kinds of quasiparticles.

D-VII.7 17:00-17:20

DETERMINATION OF THE CRYSTALLOGRAPHIC ORIENTATION IN PbTiO_3 EPITAXIAL FILMS USING OPTICAL SECOND HARMONIC GENERATION, E.D. Mishina, N.E. Sherstyuk, E.Ph. Pevtsov, A.S. Sigov, and O.A. Aktsipetrov, Moscow Institute of Radioengineering, Electronics and Automation, Moscow 117454, Russia, A.M. Grishin, Royal Institute of Technology, Stockholm, Sweden

PbTiO_3 epitaxial films have potential application in microelectronics as nonlinear dielectrics that can be used for non-volatile memory elements and arrays. Reduction of the size of the electronic devices requires a reliable tool for their diagnostics. We suggest here a techniques for nonlinear optical diagnostics of thin epitaxial films, that is based on the second harmonic generation (SHG) and can be applied "in situ" during preparation. The SHG techniques being extremely sensitive to any changes of the crystal symmetry allows one to study the film local crystallographic orientation with the spatial resolution (several microns for in-plane direction and several atomic layers in thickness) and accuracy that exceed these characteristics for conventional techniques. We report here the results of the SHG diagnostics of thin epitaxial PbTiO_3 films on YBaCuO/LaAlO_3 substrate with the use of a femtosecond Ti-Sapphire laser.

D-VII.8 17:20-17:40

SPECTROSCOPIC STUDY OF NANOCRYSTALLINE TiO_2 THIN FILMS GROWN BY ATOMIC LAYER DEPOSITION, A. Suisalu, J. Aarik*, H. Mändar*, I. Sildos, Institute of Physics, University of Tartu, Riia 142, 2400 Tartu, Estonia, *Institute of Material Science, University of Tartu, Tähe 4, 2400 Tartu, Estonia

Photoluminescence properties of thin ALD-grown TiO_2 films with different crystal structure [1] were investigated. Reflection high energy electron diffraction (RHEED), X-ray diffraction (XRD) and Raman spectrometry studies show that all the films are polycrystalline. The average crystallite size in anatase films did not exceed 60 nm while the size of crystallites with rutile structure reached 65 nm at film thickness of 150 nm already. TiO_2 -II and anatase structures were preferably formed in the beginning of growth process while rutile started to dominate after reaching of certain film thickness.

At cryotemperatures photoluminescence spectra different films were measured using resonant Ar⁺ laser light excitation (351 or 333 nm). In the spectra of anatase films measured at low temperature, in addition to recombination emission of self-trapped excitons (peak maximum at 2.4 eV), additional emission lines at 3.31 and 3.37 eV have been detected. The same lines were present in the spectra of the films which according to RHEED-data contained pure TiO_2 -II phase at the outermost surface. However, the concurrent existence of different phases inside the films was very probable in the latter case. The analysis of all experimental data enabled us to propose that the emission peaks at 3.31 and 3.37 eV can be related to exciton emission of nanocrystallites (of anatase or TiO_2 -II structure).

1. J. Aarik et al., J. Crystal Growth **181** (1997) 259.

Friday, June 19, 1998
Vendredi 19 Juin 1998

Morning
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SESSION VIII - Vertical MOS Transistor

Chairpersons: M. Van Rossum, IMEC, Leuven, Belgium

K.L. Wang, University of California, Los Angeles, CA, USA

D-VIII.1 9:00-9:40 - Invited - **THE VERTICAL HETEROJUNCTION MOSFET**, K. De Meyer*, M. Caymax, N. Collaert, R. Loo, P. Verheyen, IMEC, Kapeldreef 75, 3001 Leuven, Belgium, *also KU Leuven, ESAT-INSYS, Kard. Mercierlaan 94, 3001 Leuven, Belgium
In scaling down the classical planar MOSFET, 2 major restrictions are encountered, being lithography for the channel definition and drain induced barrier lowering (DIBL). The novel vertical heterojunction MOSFET, circumvents these problems by first using a vertical architecture where source, channel and drain areas are epitaxially grown on top of each other. As such the channel length is defined by epitaxy instead of lithography. Second the DIBL effect is avoided through the use of an heterojunction for the source/channel diode. This heterojunction introduces a natural material-defined barrier which can not be decreased by the drain action. This results in an as required low off-state current. The on-state current however is produced through the gate action which lowers the effective barrier seen by the carriers in this regime. The heterojunction consists of SiGe/Si for the PMOS and SiGe/Ge for the NMOS. The realisation of this transistor involves fundamental research on the layers to be grown, since very thin (down to 30 nm) layers are needed together with very steep gradients in both doping and composition. Also work is undertaken for the realisation of buffer layers needed to realise NMOS structures.
In the paper emphasis will be put on the device (Ion, Ioff, Vt, S, gm) and technological aspects (process description) of this new transistor. Also some words will be spent on the analytical and numerical modelling and simulation of the device.

D-VIII.2 9:40-10:00 **SELECTIVELY GROWN VERTICAL Si MOS TRANSISTOR WITH REDUCED OVERLAP CAPACITANCES**, D. Klaes, J. Moers, A. Tonnesmann, S. Wickenhauser, L. Vescan, M. Marso, M. Grimm and H. Luth, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
We have investigated the device characteristics of a novel vertical MOSFET layout. This concept is based on selective epitaxial growth and offers the advantages of achieving short channel lengths and high integration densities while still using optical lithography to define lateral dimensions. Compared to other vertical concepts, this layout has reduced gate to source/drain overlap capacitances which is necessary for high speed applications.
By means of Low Pressure Chemical Vapour Deposition a p-n-p doped Si layer has been selectively grown into a SiO₂-PolySi-SiO₂ layer package which is isolated by the vertical gate oxide. So the polysilicon only covers the channel region. The channel length is defined by the thickness of the n-doped layer and can be reduced far into the sub 100 nm region. Compared to vertical layouts using blanket epitaxy we avoid the degradation of the Si-SiO₂ interface due to RIE-etching of the silicon.
First measured device characteristics show a transconductance of 90 mS/mm for a nonoptimized p-channel MOSFET with 130 nm channel length and a 12 nm thick gate oxide. The cut-off frequencies $f_T=2.3$ GHz and $f_{max}=1.1$ GHz indicate the suitability of this device for future CMOS technology.

10:00-10:30

BREAK

D-VIII.3 10:30-10:50 **INFLUENCE OF DOPING PROFILES ON THE ELECTRICAL CHARACTERISTICS OF VERTICAL SUB-100nm-TRANSISTORS**, F. Kaesen, K.G. Anil, C. Fink, W. Hansch, I. Eisele, Universität der Bundeswehr München, 85577 Neubiberg, Germany
Vertical transistors with channel lengths down to 30 nm were fabricated on the sidewalls of mesas, which were produced by dry chemical etching of MBE grown layers. MBE offers the possibility to realise new channel doping concepts and investigate systematically the influence of these doping profiles in comparison to conventional homogenous doping on the electrical behaviour of these devices.
The concept of the planar doped barrier using delta layers embedded in intrinsic silicon is compared to the conventional homogenous doping, which is normally used in all planar transistors. It will be shown that confining the dopants on atomically sharp layer the scattering rate in the channel is reduced resulting in higher transconductance and higher electron velocity. Devices with channel lengths below 100 nm show even at room temperature distinct velocity overshoot. For these devices the electron transport mechanism approaches already at room temperature ballistic transport.
The influence of the position of the delta doping layer in the channel was investigated with respect of sub-threshold behaviour, transconductance saturation behaviour and break down voltage. These parameters can be optimized with the position of the delta layer and thus the device performance can be further increased.

D-VIII.4 10:50-11:10

COMPARISON OF LATERAL AND VERTICAL Si-AND SiGe-MOSFETS WITH ULTRA SHORT CHANNELS, D. Behammer, M. Zeuner, G. Höck, T. Hackbarth, J. Herzog, M. Schäfer*, Daimler-Benz Research Center Ulm, PO Box 2360, 89013 Ulm, Germany ; *CADwalk, Stegäckerstr. 7, 89604 Allmendingen, Germany

The fabrication of the vertical MOSFET is compatible to a standard CMOS technology with lateral MOSFETs. Process modules like gate oxidation, polysilicon gate contact, oxide spacer, contact implantation, salicidation, isolation and metallization were used for the integration of lateral and vertical Hetero- and HomomOS devices. For the vertical device the epitaxy of the drain-channel-source layer stack and the mesa etching are new processes. The definition of the field oxide depends on the position of the layer growth into the process flow. For a 100nm vertical n-MOSFET ($N_A=1 \times 10^{18} \text{cm}^{-3}$) with a 5nm thick thermal oxide we receive $g_m=375 \text{mS/mm}$ ($U_{DS}=2\text{V}$), $U_T=0.3\text{V}$, $S=80 \text{mV/dec}$ and $I_{Dmin}=1 \times 10^{-10} \text{A/}\mu\text{m}$. For a first order calculation based on a drift diffusion model (ATLAS) we get $g_m=390 \text{mS/mm}$ ($U_{DS}=2\text{V}$), $U_T=0.34\text{V}$, $S=91 \text{mV/dec}$ and $I_{Dmin}=1 \times 10^{-10} \text{A/}\mu\text{m}$. In addition we fabricated lateral n-MOSFETs with the same process modules. For a $0.5 \mu\text{m}$ lateral n-MOSFET with a 5nm gate oxide we get following measured (simulated) data: $g_m=270 \text{mS/mm}$ @ $U_{DS}=2\text{V}$ (340mS/mm), $U_T=0.34\text{V}$ (0.38V), $S=85 \text{mV/dec}$ (66mV/dec) and $I_{Dmin}=1 \times 10^{-12} \text{A/}\mu\text{m}$. The material-system Si_xGe_x is the only heterosystem that is compatible with Si devices. The vertical and the lateral MOSFET can be optimized with respect to the DIBL and the mobility by the incorporation of Ge. Simulations, device concepts and measurements will be presented.

D-VIII.5 11:10-11:30

NEW VIRTUAL SUBSTRATE CONCEPT FOR VERTICAL MOS TRANSISTORS, E. Kasper, K. Lyutovich, M. Bauer and M. Oehme, University of Stuttgart, Institut für Halbleitertechnik, Pfaffenwaldring 47, 70569 Stuttgart, Germany

Adjustment of lattice constants of SiGe active layers is usually performed by virtual substrates with SiGe relaxed buffer layers on Si substrates. The present buffer layers are either too thick or plagued by high threading dislocation density.

We propose a new concept of thin SiGe virtual substrates. Interactions of point defects with dislocations play a key role in this concept. Being introduced in the thin SiGe buffer layers during their growth, point defects, first, cause dislocations to climb which helps to annihilate threading dislocation arms with opposite Burgers vectors. Second, condensation of point defects results in prismatic dislocation loops inside the layers which avoids nucleation from the surface sites. In consequence, point defects reduce the density of existing threading dislocations and prevent the generation of new ones. This solution should allow to form virtual substrates with thin relaxed SiGe buffer layers and low threading dislocation density.

In this paper, we explain how point defects can be injected using modified MBE process techniques. These techniques utilize either the injection of low energy Si^+ ions or supersaturation of point defects resulting from very low temperature growth ($T=250^\circ\text{C}$).

D-VIII.6 11:30-11:50

OPTICAL AND ELECTRICAL CHARACTERIZATION OF Si/Ge LAYERS FOR VERTICAL SUB-100 nm MOS TRANSISTORS, X. Zhang and P. Unelind, Department of Solid State Physics, Box 118, 22100 Lund, Sweden and J. Olajos, Physics Department, S. Qaboos University, PO Box 36, Al-Khoud 123, Oman

n- and p- VAHMOS (Vertical Advanced Heterostructure MOS) transistors, Si/Ge alloy-layer pseudomorphically to Si on a relaxed buffer have been grown by Molecular Beam Epitaxy (MBE) and Chemical Vapor Deposition (CVD).

Modulation doped CVD samples with a SiGe channel of 15 nm two 25 nm Si-spacers and doping concentration of $1-5 \times 10^{18} \text{cm}^{-3}$ were studied by means of photoluminescence and photocurrent spectroscopy. Signals from SiGe-layers were observed from samples grown at 625°C with Ge content of 10%. From the measured bandgap energies a fully strained configuration, with layer thicknesses close to the nominal were determined.

Considerably higher Ge-contents were used in MBE samples. Optical measurements confirm the X-ray analysis indicating absence of disorder and relaxation for Ge-contents up to 43%. Calculated and experimentally determined bandgap energies showed that the Ge-content for the MBE grown layers are within 3% accuracy as compared to nominal values.

A defect level in the MBE-grown samples with an activation energy of about 0.58 eV was identified by Deep-Level Transient Spectroscopy (DLTS).

12:10-14:10

LUNCH

SYMPOSIUM D

Friday, June 19, 1998
Vendredi 19 Juin 1998

Afternoon
Après-midi

SESSION IX - Poster Session III: Analysis

14:10 - 15:30 See programme of this poster session p. D-27 to D-32.

END OF SYMPOSIUM D

SYMPOSIUM D

SYMPOSIUM D
POSTER SESSIONS

Tuesday June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-midi

SESSION III - Poster Session I: Selfassembly and Strain Adjustment
16:00 - 18:00

- D-III/P1** GROWTH OF Ge ON H-TERMINATED Si (111) SURFACE, K. Ishii, H. Kuriyama, S. Matumoto, Dept. of Elec. Eng., Keio Univ., Hiyoshi, Yokohama 223, Japan
The film-growth on H-terminated Si surface is different from the growth on a clean Si surface and an effect of H is dependent on the kind of film. Growth of Ge on the H-terminated Si(111) surface as well as on the clean surface has been studied using UHV-scanning tunneling microscopy (STM).
Si (111) substrates were dipped into a 1% HF solution and were terminated with dangling bonds linked to H atoms. Germanium was evaporated at room temperature using electron gun evaporator in UHV chamber and the sample was annealed subsequently at 400°C~600°C for 5 minutes. After 400°C annealing, at the coverage of 1~2ML, Ge on H-terminated Si surface did not form a 2-dimensional layer which is normally observed on the clean surface, but formed many small islands on terraces. At the coverage of 3~5ML, Ge surface had a lot of roughness. It means that hydrogen of Si surface remains at Ge/Si interface at 400°C, preventing Ge from diffusing on Si surface. After annealing at 600°C, the critical thickness of Ge on a H-terminated Si surface increased more than that of Ge on a clean surface due to hydrogen desorption from Ge growth layer.
- D-III/P2** TEM STUDY OF THE FORMATION OF InAs SELF-ASSEMBLED QUANTUM DOTS IN GaAs, E. Müller*, E. Ribeiro**, T. Heinzel**, K. Ensslin*,**, G. Medeiros-Ribeiro, and P.M. Petroff; Materials Department, University of California, Santa Barbara, 93106 California, USA; *Labor für Mikro- und Nanostrukturen, Paul-Scherrer Institut, 5232 Villigen, Switzerland; **Laboratorium für Festkörperphysik, ETH-Zürich, 8093 Zürich, Switzerland
The formation of MBE-grown InAs quantum dots on GaAs was structurally characterized by several methods. The InAs dots were overgrown by 3nm of GaAs and subsequently covered by a thick AlGaAs layer. In dependence of the initial InAs layer thickness, a transition from an InAs wetting layer to the formation of InAs dots having a diameter of 10-20nm was observed by cross-sectional transmission electron microscopy. In samples with high In-content, however, not only simple dots were observed but a sandwich-like three-layer contrast. In the dot regions the measured lattice constants indicate a InAs-like, a GaAs-like and again an InAs-like layer just below the AlGaAs cap. The dots are free of defects. The occurrence of the unexpected three-layer contrast is most likely related to the previously observed vertical self-alignment of InAs dots.
- D-III/P3** RELATION OF INITIAL THIN FILM FORMATION TO DEFECTS INDUCED BY LOW ENERGY IONS, H. A. Durand, K. Sekine, K. Etoh, K. Ito, I. Kataoka, Japan Aviation Electronics Industry Ltd, Central Research Laboratory, Musashino 3-1-1, Akishima-shi, Tokyo 196-8555, Japan
We introduce here our last results* on the UHV-STM study of the initial thin film formation deposited by low energy ion beam on HOPG. Despite most defect may appear as similar perturbation of the electronic partial density on STM high resolution images, by analyzing the symmetry of perturbation patterns we were able to identify several categories of defects and discriminate between adsorbed atoms, single and multiple vacancies and interstitials. For the purpose of comparison of their influence on the formation of nano-islands, films were grown by two methods: first by using low energy ions of carbon and nickel at high density (up to 50 ions/nm²), and second, by using molecular jets of nickel and other metals. Particularly, we investigate the role of defects induced by ions on the size, density and structure of islands. We reveal several modes of coalescence in the Stranski-Krastanov class of growth. Finally, we show how low energy ion beams enables the control of size, density and structure of self assembled nanoparticles on a substrate.
*Partial results were reported at the MRS'97 Fall Meeting Symposium A, Boston.
- D-III/P4** ROLE OF HYDROGEN DURING Si CAPPING OF STRAINED Ge OR Si_{1-x}Ge_x HUT CLUSTERS, D.Dentel, J.L.Bischoff and L.Kubler, LPSE, Université de Haute Alsace, 68093 Mulhouse, France
Atomic hydrogen (H) is supplied during Si capping (by solid source MBE at 400 or 500°C) of Ge related islands strained on Si(001). Without H, Si capping is known to smooth the initial rough surface caused by the Stranski-Krastanov Ge growth mode and ensuring a partial strain relief at the island crests. We have previously shown that this smoothing takes place by stress mediated surface diffusion of Si accumulating in the troughs between the hut-clusters where the misfit is the lowest, and by Ge segregation. The effect of H is now, in reducing these surface migrations, to maintain the initial roughness as proved by the persistence of spotty RHEED patterns and the non-restoration of intensity oscillations. Moreover, the a_{||} recovery of the Si bulk value in the Si cap layer is much slower than without H, a consequence of the kinetically blocked Si deposition, particularly on the top of the partially relaxed hut clusters where it is forced to grow more tensely strained than without H. As a general learning, the same H adsorption and adatom mobility decrease is able to preserve here the initial Ge related 3D growth while, for the growth of Ge upon Si, it maintains a 2D growth in preventing 3D island formation. In both cases the kinetic limitation impedes local elastic energy minimizing and immediate strain relief. These trends may be of importance in preparing quantum dots by self assembling of Ge hut clusters.
- D-III/P5** CLUSTER-SIZE DISTRIBUTION OF SiGe ALLOYS GROWN BY MBE, N. Pinto, R. Murri, INFN Dipartimento di Matematica e Fisica, Università di Camerino, Via Madonna delle Carceri, 62032 Camerino, Italy; R. Rinaldi, INFN Dipartimento di Scienze dei Materiali, Università di Lecce, Via Arnesano, 73100 Lecce, Italy
Cluster-size distributions of Si_xGe_{1-x} alloys were statistically analyzed. The samples were grown by MBE on Si(100) as a function of the growth temperature, composition (x) and thickness changing only one parameter at a time. The samples were investigated by both electron microscopy (SEM and TEM) and atomic force microscopy (AFM). The microscopy observations revealed the formation of irregular islands, Stranski-Krastanov grown on Si(100), whose size-distribution had a bimodal structure with an initial power-law decrease, superimposed on a bell-shaped distribution peaked around the mean cluster size. We found that the values of the power-law exponent and the peak position change with the growth parameters.
We explain the Si_xGe_{1-x} cluster-size distribution in terms of a modified Family-Meakin (FM) model.

- D-III/P6** STRUCTURE AND DYNAMICAL PROPERTIES OF Ge NANOCRYSTALS EMBEDDED IN SiO₂ FILMS, A.G.Rolo, M.J.M. Gomes, Departamento de Fisica, Universidade do Minho, Largo do Pago, 4709 Braga Codex, Portugal, O. Conde, Departamento de Fisica, Universidade de Lisboa, Campo Grande, 1700 Lisboa, Portugal and M.I. Vasilevskiy, Institute for Physics of Microstructures, RAS, 603000 Nizhni Novgorod, Russia
SiO₂ films containing small particles of Ge were grown by magnetron rf-sputtering. The films were characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. XRD studies revealed diamond structure of Ge particles in the films grown at temperatures higher than 500°C, and the relative intensities of the diffractogram peaks indicated random orientation of the particles. From the linewidth, the mean diameter of the Ge nanocrystals was estimated to vary between 30 and 80 Å, depending on growth conditions. XPS measurements showed that the nanocrystals were very little oxidised.
Raman spectra of the films, taken using an Ar laser, showed broadened peaks due to Ge TO phonons. For the films with nanocrystalline Ge, such a peak was relatively narrow and downshifted a little bit with respect to the bulk Ge TO frequency. Its lineshape was rather asymmetric. It could be fitted fairly well using a model considering TO-type phonon modes confined in nanocrystalline spheres. Particularly, the confined modes with $l=0$ and $n>1$, l and n being the spherical quantum numbers, are responsible for the low-frequency wing. The values of the mean diameter obtained by this fitting agree with those estimated from the XRD data.
- D-III/P7** GROWTH OF III-V SEMICONDUCTOR LAYERS ON Si PATTERNED SUBSTRATES, T.Ya. Gorbach, R.Yu. Holiney, L.A. Matveeva, P.S. Smertenko, S.V. Svechnikov, E.F. Venger, ISP NASU, prospekt Nauki, 45, 252028 Kyiv, Ukraine, R. Chiah, M. Faryna, IMMS PAS, 25 Reymonta ul., 30059 Krakow, Poland
Patterned unheated Si(100) substrates have been found to be effective for a pulse vacuum thermal deposition (pulse-VTD) of GaAs and GaP thin layers (50-500 nm).
The morphology, the composition and the crystallinity of GaAs and GaP layers were characterized by scanning electron microscopy, electron X-ray analysis and electron diffraction technique. Two different substrate morphologies preparing by chemical dissolution have been used: convex (the regular tetragonal pyramids) and concave (structure like semispherical plates). The pyramid faces and the plate surfaces contained a number of nanometers size patterns associated with the terraces, steps, kinks, entering angles, triangle grain contours which were the active sites for material condensation.
It is shown that the growth process in the step flow and the kink flow regimes when the layer morphology followed the substrate morphology leads to epitaxial growth. In the morphological instability regime the columnar structure formation and Ga precipitation are detected. The effect of the pulse-VTD technological parameters, the dimension and shape of substrate patterns in the analysing of the observed results have been discussed.
- D-III/P8** THE INFLUENCE OF CARBON ON THE SURFACE MORPHOLOGY OF Si(100) AND ON SUBSEQUENT Ge ISLAND FORMATION, R. Butz and H. Lüth, Institute of Thin Film and Ion Technology (ISI), Research Centre Jülich, 52425 Jülich, Germany
The surface structure of Si(100) after carbon deposition has been studied mainly by scanning tunneling microscopy (STM) at a substrate temperature of 600°C. At carbon coverages below 1/2 monolayer (ML) a c(4x4) structure is obtained. Higher coverages (up to 1ML) give rise to island formation and a 2x1 structure of the substrate surface. The surface after subsequent Si epitaxy is documented and depends on the initial carbon concentration. The original c(4x4) structure can be observed even after additional 3nm thick epitaxial Si layers.
The island formation of Ge on Si(100) at 600°C after carbon (1/4ML) adsorption leads to a reduction of the critical layer thickness and very small islands of about 5nm in diameter. With increasing Ge concentration additional „hut clusters“ (about 20nm diameter) appear. The (105) facets of the hut clusters are also found in reduced extent for the small islands grown on a rough (2x8) like substrate structure.
- D-III/P9** MECHANISMS OF ELASTIC ENERGY MINIMIZATION DURING Si CAPPING OF STRAINED Ge or Si_{1-x}Ge_x HUT ISLANDS: TEM AND RHEED STUDIES, D. Dentel, J.L. Bischoff, L. Kubler, LPSE, Université de Haute Alsace, 68093 Mulhouse Cedex, France and C. Ghica, C. Uhlaq-Bouillet, J. Werckmann, IPCMS, 23, rue du Loess, 67037 Strasbourg, France
The hut cluster formation during Ge or Si_{1-x}Ge_x SSMBE growth on Si(001) is a well known kinetic pathway for partial strain relief. It results in undulated morphologies with {105} facets allowing a lattice parameter relaxation on the island apexes as determined by RHEED. The present paper is intended to elucidate how a subsequent Si coverage avoids to be tensile strained and impedes further increase of stored elastic strain energy. As proven by different TEM, HRTEM and RHEED studies, the relevant mechanisms are governed by a combination of Si and Ge surface diffusions. When high growth kinetics quench the Ge segregation and limit chemical strain relief, only fast Si surface diffusion takes place, mediated by stress variations on the non capped island curvatures. Si is depleted from the top of the islands and accumulates in the troughs of the ripples where it is accommodated mostly unstrained. By this selective Si uptake, the surface undergoes a rapid smoothing and a_s recovery towards the Si bulk value. In the finally buried Ge related islands the strain, dictated by the Si buffer, ends by being exclusively along the growth direction or tetragonal ($\Delta a_{||}=0$). Conversely, if the Si surface diffusion is blocked, more island induced strain will spread in the Si cap-layer.
- D-III/P10** PHOTOLUMINESCENCE STUDY OF In As/GaAs SELF-ORGANISED QUANTUM DOTS GROWN BY MBE, M. Hjiri, F. Hassen, H. Maaref and R. Murray*, Laboratoire de Physique des Semiconducteurs, Département de Physique, Faculté des Sciences de Monastir, 5000 Monastir, Tunisia; *IRC, Semiconductor Materials, Imperial College, London SW2BZ, UK
In recent years much attention has been devoted to the fabrication and application of self-organised quantum dots in fields of optoelectronics and lasers. Most of self-organised quantum dots (QDs) have been fabricated by the Stranski-Krastanow (SK) growth method. Many studies of QDs in GaInAs/GaAs and InAs/GaAs systems on (100)-oriented GaAs substrates, show that there is a critical thickness layer of InAs (1.7 atomic monolayer) from which QDs can exist.
In this communication we present our results of photoluminescence (PL) obtained on four samples of InAs/GaAs grown by MBE with InAs layer width ranging from 0.5 to 2 ML. In samples of InAs width less than 1.7 ML, PL lines of quantum dots like structures were observed, which are in agreement with those obtained by Patané et al where they had seen QDs in 0.6ML InAs/GaAs samples. In the same samples the PL lines from QDs change in shape and show a red shift in time. This phenomenon is due to the relaxation and the rearranging of QDs. It was observed recently by AFM (sample without caplayer) in InP/Gap and in CdSe/ZnSe QDs. The QDs PL lines of 2ML InAs width sample never show any change even in shape and position.
In conclusion, we can say that the critical layer thickness has no limit but samples less than 1.7ML are not stable in time.
- D-III/P11** COMPOSITION, STRESS AND STRUCTURE OF Ge ISLANDS GROWN ON Si <100>, D. V. Regelman, V. Magidson, R. Beserman, Solid State Institute and Physics Department, Technion, 32000 Haifa, Israel, K. Dettmer, Institute of Semiconductor Physics and Optics, Technical University, Braunschweig, Germany
We investigated the Ge islands epitaxially grown on (100) Si substrate. AFM measurements were performed to investigate the size and geometry of these islands. Two main types of islands were found: a 200-300nm base and 100nm height small islands and 2-3µm base and 150nm height large islands. A well resolved multy facet structure of small islands was measured by AFM.
Micro Raman technique was used to investigate the strain and composition of the islands. Using a confocal setup with XY translator we resolved a Raman scattering spectra of a single island. A Raman scattering was measured during a scan over a large island. This enabled us to map the Si distribution change inside this island. We found a high Si content (~30%) inside the originally Ge grown island. Si concentration inside small islands is much lower than in large islands due to lower diffusion coefficient of Si from the substrate.

- D-III/P12** STRAIN AND SHAPE OF SELF-ASSEMBLED QUANTUM DOTS STUDIED BY GRAZING INCIDENCE X-RAY TECHNIQUES, I. Kegel, T.H. Metzger, P. Fratzl, A. Lorke and J. Peisl, University Munich, Sektion Physik, Geschwister-Scholl Platz 1, 80539 Munich, Germany

Information on shape and strain distribution of dislocation-free quantum-dots grown in the Stranski-Krastanov mode is crucial for adequate performance of related devices. The validity of different growth models has to be tested against experimental data on the final structure of the dots. We have investigated naked InAs dots on GaAs (100) by grazing incidence small angle scattering (GISAXS) and grazing incidence diffraction (GID) in which the depth probed was limited to about 10nm only. From GISAXS we find the average radius of cylindrical dots to be 15nm. Strain is most easily measured with diffraction experiments (GID). We introduce a new concept of „iso-strain-scattering“ which enables us to reveal detailed information on the interdependence of shape and strain in coherent InAs islands. From three-dimensional reciprocal space mappings, we extract the relationship between the radius of the dots and the relaxation which was found to be linear. The relaxation in the InAs island ranges from pseudomorphically strained at the bottom of the island to completely relaxed at the top. In addition, the local strain gradient at any relaxation in the dot is obtained.

For InAs dots buried under 4nm GaAs we find elliptically shaped objects ($a=90.2$ nm, $b=62.6$ nm) with a hole in the center which we like to call „quantum donuts“.

- D-III/P13** TEM STUDY OF SELF-ORGANIZATION PHENOMENA IN CdSe FRACTIONAL MONOLAYERS IN ZnSe MATRIX, A. Sitnikova, S.Sorokin, T.Shubina, I.Sedova, A.Toropov, S.Ivanov, Ioffe Physical-Technical Institute, 194021 St.Petersburg, Russia, M.Willander, University of Gothenburg/Chalmers University, 412 96 Gothenburg, Sweden

In spite of a great interest in the II-VI low-dimensional nanostructures, there is a lack of experimental data on the self-organization phenomena in these materials. In this paper, self-organization of CdSe fractional monolayers (FM) with a nominal thickness in-between 0.1-3.0 monolayer (ML) in ZnSe ($\Delta a/a \sim 7\%$) has been investigated by TEM. The CdSe/ZnSe nanostructures are grown by both conventional MBE and migration enhanced epitaxy (MEE) techniques. It has been shown that MBE growth mode is characterized by the more pronounced CdSe ordering. The evolution of CdSe atomic ensembles from the 2D-islands coherent with matrix, through the large 2D-islands accompanied by the specific defects due to relaxation of adjacent ZnSe to the 3D-clusters has been observed. The mechanisms of self-organization phenomena in CdSe FMs at different growth modes are analyzed. The transformation of the FM structure is correlated with the results of PL study of the samples (energy positions and widths of the PL lines).

- D-III/P14** STUDY OF InAs QUANTUM DOTS IN GaAs PREPARED ON MISORIENTED SUBSTRATES, E. Hulicius, J. Oswald, J. Pangrac, K. Melichar, T. Simecek, Institute of Physics, Academy of Sciences Cukrovarnicka 10, 162 53 Prague 6, Czech Republic

Technological conditions for Stranski-Krastanow growth of Quantum Dots (QD) in the InAs/GaAs system using Low Pressure Metal-Organic Vapour Phase Epitaxy (LP-MOVPE) are described. Properties of this already classical A^{III}B^V material system for self-organized QD formation depend not only on the thickness of the Wetting Layer (WL), growth rate, layer growth interruption time (for the development of dots), but also on the AsH₃ partial pressure (influencing V/III ratio) in the reactor during the growth of WL and QD formation period and on the substrate orientation.

Photoluminescence (PL) of QDs prepared under different conditions on GaAs substrates with different crystallographic orientation has been measured at several temperatures between He and room temperatures.

Strong dependence of PL intensity on V/III ratio as well as on slight substrate misorientation was observed. The intensity of the room temperature QD luminescence is at least 10 times higher for all samples prepared on the exactly (100) orientated substrates than on the (100) 3° towards (110) substrates. Non-monotonous behaviour of the temperature dependence of PL intensity confirms the existence of a barrier for holes between the WL and QDs.

The influence of substrate misorientation on the self-organization of the QDs is discussed.

- D-III/P15** ALUMINUM NANOSTRUCTURES BY THERMAL AND STM-INDUCED CVD, E. Boellaard, C. Bisch, G.C.A.M. Janssen, Delft University of Technology, DIMES/S, Lorentzweg 1, 2628 CJ Delft, The Netherlands

Small metallic structures of aluminum have been produced by thermal decomposition of dimethyl aluminum hydride (DMAH) in an ultra high vacuum compatible reactor system. It turned out that aluminum can be deposited selectively onto silicon within a silicon dioxide mask. Special attention was put onto the nucleation stage of the aluminum nuclei and the subsequent growth. The elongated aluminum crystallites and pyramids, which are in the 30 to 1000 nm range, show distinct epitaxial relations with the silicon substrate. By SEM and AFM it was observed that the crystallites grow in a direction following the orientation axis of the Si(111) substrate surface. This effect offers attractive prospects for the production and stabilisation of aluminum nanostructures with well defined geometries. On silicon oxide substrates, free, well developed 3D crystals are grown with a slower kinetic rate. The size of these crystallites ranges from 30 to 3000 nm. We will use the same chemistry but improve the lithography by using a scanning tunnelling microscope (STM) to create patterns in the nanometer range. In an other approach, aluminum structures will be directly written with the STM by decomposing pre-adsorbed DMAH at room temperature.

- D-III/P16** EPITAXIAL GROWTH AT HIGH RATES WITH LEPECVD, C. Rosenblad, H. von Känel, ETH Zürich, 8093 Zürich, Switzerland and J. Stangl, G. Bauer, Institut für Halbleiterphysik, Johannes Kepler Universität Linz, 4040 Linz, Austria

Low energy DC-plasma enhanced chemical vapor deposition (LEP- ECVD) has been shown to be an alternative growth technique for SiGe heteroepitaxy, with crystal quality conforming to the state of the art at growth rates in the range of 1Å/s[1]. We have now studied the crystal quality of the epitaxial films as a function of the plasma intensity. These studies show that even at a discharge current of 70 A, which is the highest discharge current possible in our setup, no plasma damage occurs provided that the ion energy is kept below 15 eV. With this high plasma discharge current, corresponding to a huge plasma density, epitaxial Si films exhibiting etch pits densities below 10⁻⁶cm⁻² have been obtained at growth rates exceeding 1 nm/s. We have applied LEPECVD to the synthesis of relaxed SiGe alloy buffers which have to be several μm thick in order to be used as virtual substrates for strained Si quantum wells in the n-channel SiGe MODFET.

[1] C. Rosenblad et al., E-MRS 1998 Spring Meeting, to be published in Thin Solid Films.

- D-III/P17** STRUCTURAL CHARACTERISATION OF SiGe STEP GRADED BUFFER LAYERS GROWN ON PRE-STRUCTURED Si[001] SUBSTRATES BY MOLECULAR BEAM EPITAXY, E. Müller, R. Hartmann, Ch. David, D. Grützmacher, Labor für Mikro- und Nanostrukturen, Paul-Scherrer Institut, 5232 Villigen, Switzerland

Transmission electron microscopy (TEM) as well as atomic force microscopy (AFM) were applied in order to study the effect of prestructured Si substrates on a subsequently grown SiGe graded buffer layer. Using e-beam lithography square and line shaped mesas were defined at angles of 0°, 15°, 30° and 45° towards the [110] crystallographic orientation. The structures were overgrown by molecular beam epitaxy with step graded buffer layers up to a Ge concentration of 25%. The effect of the width and the crystallographic orientation of the line shaped mesas on the dislocation density has been studied in detail by TEM and AFM. Besides a faceting at the edges of the mesa structures, a strong effect of the width and of the orientation on the dislocation density has been observed.

- D-III/P18** TEM INVESTIGATION OF THE DEPENDENCE OF STRUCTURAL DEFECTS ON PRELAYER FORMATION OF GaAs-ON-Si THIN FILMS, Ch.B. Lioutas, A. Delimitis and A. Georgakilas, Aristotle University of Thessaloniki, Department of Physics, 54006 Thessaloniki, Greece
The study of the structural characteristics of GaAs-on-Si heterostructures and their dependence on the specific growth conditions is of great importance, since they are the main factor that controls the quality and reliability of Si based optoelectronic devices. In this work, we show the dependence of structural defects (threading dislocations, anti-phase boundaries, twins) on the kind (Ga or As) and the growth temperature of the prelayer in GaAs/Si samples, using Transmission Electron Microscopy methods. GaAs films were grown by Molecular Beam Epitaxy on tilted (100) vicinal Si substrates, with tilting angles varying from 0° to 9° and exposing the Si substrate to As or Ga at 400°C and 750°C. In all cases, the main characteristic is that the density of threading dislocations does not change dramatically, being in the order of 10^6 cm^{-2} . The specific growth conditions do not also affect specimens grown on Si substrates with tilting angle equal to 4.5°. In contrast, for samples with small tilting angles (0.5° and 1.5°) the observed twins or microtwins are disappeared when the growth temperature of prelayer changes. On the other hand in the case of great tilting angles (7.5° and 8°), the existence of extended planar defects is driven not by the prelayer growth temperature, but by the different GaAs direction of growth -relevant to Si misoriented substrate- and the kind of prelayer.
- D-III/P19** STM STUDY ON STEP GRADED $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(001)$ BUFFERS, M. Kummer, B. Vögeli, and H. von Känel, Laboratory for Solid State Physics, HPF F15, 8093 Zürich, Switzerland
We report on the surface structure of step graded $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(001)$ buffers, which are presently being used as virtual substrate for modulation doped quantum well structures (MODQW). Despite the enormous progress in the past few years, strain relaxation mechanisms are still not completely understood. The samples in this study were grown by means of rf magnetron sputter epitaxy (MSE). It has been demonstrated, that MSE can be used to grow $\text{Si}/\text{Si}(001)$ of high crystal quality, suitable sputter conditions provided[1]. The surface structure of the compositionally graded $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(001)$ buffers was measured with a scanning tunneling microscope (STM). The study was performed by varying three essential growth parameters: the substrate temperature, the steepness of the grading and the final concentration x of the buffer. The evolution of the typical cross hatched surface was monitored after each increment of x by 0.05. Our findings are, that even for small Ge concentrations, the surface diffusion length is dramatically decreased, which leads to 2D island growth. The influence of the grading steepness is tremendous. The rms roughness of the surface appears to depend linearly on the gradient, emphasizing the importance of shallow gradients for technical applications. The surface was measured as a function of the growth temperature in the range between 370°C and 600°C. Even at the lowest temperatures, the strain was found to be partially relieved as evidenced by the formation of a cross hatch. Striking features are the Ge segregation for all temperatures, leading to the typical 2×2 surface reconstruction, and the formation of the biatomic S_2 -surface steps, perpendicular to the direction of steepest descent.
[1] B. Vögeli, S. Zimmermann, and H. von Känel, Thin Solid Films, in press
- D-III/P20** ION ASSISTED MBE GROWTH OF SiGe NANOSTRUCTURES, M. Bauer, M. Oehme, K. Lyutovich, E. Kasper, Institut für Halbleitertechnik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany
The bombardment of thin SiGe buffers with 1 keV Si^+ ions during the molecular beam epitaxy growth is a possible way for the injection of point defects in order to promote the relaxation and to reduce the dislocation density. For this purpose, the e-beam evaporator was optimized by increasing the emission current and decreasing the energy of the impinging electrons to create a high density Si^+ ion flux in our MBE system. To the isolated substrate holder a potential up to several kV can be applied to direct, focus and accelerate the Si^+ ions. A high efficiency Ge effusion cell ensures stable and controllable Ge fluxes for growth rates up to 2.5 Å/s . Under these conditions several sets of thin SiGe layers (65-300 nm) containing from 20 to 100% of Ge were grown and investigated comparatively with reference samples deposited without ions at 650°C. By the "ion growth program", after the deposition of Si buffers, SiGe layers were grown in 3 stages. First part of the layer (e.g. 1/8 of the nominal thickness) and the last one were grown without ion bombardment. Second part (e.g. 2/8 of the thickness) was deposited under 1 keV accelerated Si^+ ion bombardment. Ge content was kept constant during all three stages. Sharp interfaces and uniform Ge profiles were shown by SIMS. Strain relaxation in high Ge content layers is nearly 100% as proven by XRD. In pseudomorphic layers a bombardment may result in nucleation of stacking faults shown by TEM. AFM and preferential chemical etching of relaxed ion bombarded layers have shown higher surface smoothness and a reduction of etch pits densities by two orders of magnitude, correspondingly.
- D-III/P21** COALESCENCE OF GERMANIUM ISLANDS ON SILICON, C. Schöllhorn, M. Oehme, M. Bauer and E. Kasper, Institut für Halbleitertechnik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany
The growth of Ge islands on Si (Stranski-Krastanov growth mode) is well known. At larger Ge coverages the islands coalesce and form a quasi two-dimensional film. We investigated this transition from islands growth to quasi two-dimensional films for a rather high Ge deposition rate of 0.25 nm/s . At mean thicknesses of 1.25 nm and 3.75 nm the surface morphology of Ge depositions were observed by atomic force microscopy as function of deposition temperatures. At temperatures above 500°C - 550°C we confirm the 3-D islands growth as expected from the Stranski-Krastanov growth mode. But below these temperatures the islands coalesce and form a continuous film. The waviness of the films decrease with decreasing temperatures resulting in smooth layers at 300°C growth temperature.
- D-III/P22** DISLOCATION PATTERN FORMATION IN EPITAXIAL STRUCTURES BASED ON SiGe ALLOYS, T.G. Yugova, Institute of Rare Metals; V. I. Vdovin, M.G. Mil'vidskii, Institute for Chemical Problems of Microelectronics, B. Tolmachevsky per. 5, 109017 Moscow, Russia; L.K. Orlov, V.A. Tolomasov, A. V. Potapov, Institute for Physics of Microstructures, Nizhny Novgorod, Russia; N. V. Abrosimov, Institute of Crystal Growth, Rudower Chaussee 6, 12489 Berlin, Germany
The dislocation patterns in SiGe/Si and SiGe/SiGe heterostructures grown by molecular beam epitaxy have been studied by chemical etching/Nomarski microscopy and transmission electron microscopy. Specific subjects include the densities of misfit dislocations at the interface, threading dislocations in the epitaxial layer, and dislocations in the near-interface substrate region as functions of the SiGe alloy composition. The evolution of dislocation pattern in heterostructures during the epitaxial growth has been studied and active mechanisms of MD generation and multiplication have been determined. The dislocation pattern in heterostructures was found to form as a result of concerted operation of several mechanisms of MD generation and multiplication. The obtained results are discussed in terms of the influence of alloy composition on dislocation generation, propagation and multiplication. Special emphasis is given to the influence of the correlation between the layer and substrate plasticity upon the dislocation distribution over the three-dimensional MD network near the interface.
- D-III/P23** HETEROEPITAXY OF PbS ON POROUS SILICON, V. Levchenko, L. Postnova, Institute of Solid State and Semiconductor Physics, Brovka 17, 220072 Minsk, Belarus and V. Bondarenko, N. Vorozov, V. Yakovtseva, Belarussian State University of Informatics and Radioelectronics, Brovka 6, 220027 Minsk, Belarus
Epitaxial PbS films were grown on the surface of porous silicon (PS) formed on the silicon substrate of (111) orientation by molecular-beam epitaxy (MBE). The uniform PS layers of 5 μm thick were produced by electrochemical anodic treatment of n-silicon in HF solution. The structure of both PbS and buffer PS was studied by X-ray diffraction analysis as well as scanning electron microscopy. The PbS layer has been demonstrated to have a columnar structure at the early stages of growth, while a monolithic structure of the grown layer has been observed with the increasing a thickness of the epitaxial layer up to 0.5-1.0 μm . Comparison studies revealed that epitaxial PbS films on the PS can be obtained by MBE under optimal conditions of both PS formation and PbS epitaxial growth. The optimized PbS epitaxial layers on the Si substrate with PS buffer layers were structurally comparable with those grown on the BaF₂ substrate with matched lattice parameter.

- D-III/P24** DEFECT DISTRIBUTION AND MORPHOLOGY DEVELOPMENT OF SiGe LAYERS GROWN ON Si(100) SUBSTRATES BY LPE, A. M. Sembian, M. Konuma, I. Silier, A. Gutjahr, N. Rollbuehler, Max-Planck-Institut fuer Festkoerperforschung, Heisenbergstr 1, 70569 Stuttgart, Germany, and F. Banhart, Max-Planck-Institut fuer Metallforschung, Heisenbergstr 1, 70569 Stuttgart, Germany

The misfit strain relaxation and defect formation are one of the most important and interesting topics in the field of hetero epitaxy. Especially, the cross-hatch pattern and defect formation in the SiGe layers grown on Si(100) substrates are very interesting, considering the potential applications of both the strained and relaxed layers of SiGe. We grow SiGe layers on Si(100) substrates using Liquid Phase Epitaxy technique. The SiGe layers with different Ge content are grown at temperatures around 950°C, using different growth parameters. The cooling rates during the growth process play an important role on the development of surface morphology and defect distributions. The grown layers are characterized using various techniques like SEM, NDIC and surface profilometer in order to understand the variations of surface morphology according to the growth parameter. The microscopic morphology of SiGe layers is revealed by AFM. The defect distributions in the layers are measured using TEM and the threading dislocations are investigated by preferential SECCO chemical etching. The results of our experiments will be discussed in detail considering various aspects involved in the growth technique.

- D-III/P25** GROWTH AND ANNEALING OF CaF₂ FILMS ON VICINAL Si(111), J. Wollschläger, A. Klust and H. Pietsch, Institut für Festkörperphysik, Universität Hannover, Appelstr.2, 30167 Hannover, Germany

The quality of insulating layers used as tunneling barriers for nanoelectronic devices has to be extremely high. Their thickness of a few atomic layers must be homogeneous on a lateral scale of several μm . One well-suited candidate to fulfill these demands for Si substrates is CaF₂, due to the low misfit of only 0.5%. It is expected that the film morphology is improved if the admaterial is deposited on vicinal substrates (step flow growth) since the nucleation barrier is by-passed. Therefore we studied *in situ* the CaF₂ growth on vicinal Si(111) with a misfit of 1° by Atomic Force Microscopy (AFM). At elevated temperatures we observe that CaF₂ does not grow in the step flow mode rather it covers inhomogeneously the substrate. The CaF₂ has monolayer thickness on some terraces while the film on other terraces is several atomic layers thick. The substrate steps are diffusion barriers so that the CaF₂ grows preferentially parallel to the steps. This barrier is overcome at some sites by triangular protrusions. At low temperature the growth is changed completely to the Layer-by-Layer mode with homogeneously covered terraces except for some additional monoatomic islands. It is reported that the interface quality is improved by annealing. Therefore we studied also the annealing on the morphology of the low temperature deposited films. We observed that CaF₂ desorbs preferentially from steps so that „teeth“-like rows are formed and the film quality is not improved.

- D-III/P26** INFLUENCE OF STRESS ON GROWTH INSTABILITIES EVOLUTION ON Si SUBSTRATES, L. Lapena, I. Berbezier, CRMC2-CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France and B.A. Joyce IRCSM, Imperial College of Science, Technology and Medicine, The Blackett Laboratory, Prince Consort Road, London SW7 2BZ, UK

This paper reports on the nucleation and the evolution of growth instabilities on Si surfaces. Quantitative analysis of the morphology is performed by TEM, AFM and grazing incidence X-ray diffraction (GIXRD). Growth instabilities are evidenced during the homoepitaxial growth of Si on vicinal (from (001) to (111)) surfaces, but such instabilities do not develop on singular Si(111) surfaces. The instability leads to a sinusoidal-like morphology whose wavelength and amplitude is related to kinetic parameters (step density, growth temperature and layer thickness). When a compressive stress is applied to the growing film, the destabilization of the step train is dramatically enhanced. For example a 100Å thick Si_{0.7}Ge_{0.3} layer displays an undulation with a shape comparable to that obtained for a 5000Å thick Si film. At the atomic level, the surface shape is in fact a series of facets typical of step bunching. When the surface reaches a critical step density, the nature of the interactions between steps is changed from repulsive to attractive due to the stress induced by the step edges. In all cases, we show that the undulations orientate along the step edges on vicinal surfaces. Ultimately, the undulatory morphology which is a metastable state evolves kinetically towards a faceted equilibrium shape.

- D-III/P27** EPITAXIALLY STABILIZED ULTRATHIN Sn/Si AND Si_{1-x}Sn_x/Si QUANTUM WELL HETEROSTRUCTURE SUPERLATTICES, K.S. Min and H.A. Atwater, T.J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena CA 91125, USA

Sn-rich Si_{1-x}Sn_x alloy system is predicted to have direct and tunable energy gap for Sn composition exceeding some critical concentration. To date, growth of such structures has been hampered by the large lattice mismatch and a strong tendency for Sn atoms to segregate to the surface during growth. We report successful growth of quantum well superlattice structures of ultrathin, coherently strained Sn/Si with Sn coverage up to 1.4 ML and high Sn concentration Si_{1-x}Sn_x/Si alloy superlattice structures with Sn concentration up to 0.10 for 4nm and up to 0.25 for 1 nm Si_{1-x}Sn_x layers. Superlattice structures free of extended defects have been achieved with up to 10 periods of 1 ML Sn/6 nm Si. High Sn concentration with minimum segregation is achieved by a modified molecular beam epitaxy technique involving large modulations in substrate temperature and growth rate. Accurate measurements of the concentration and strain were made using Rutherford backscattering spectrometry and high-resolution X-ray rocking curve analysis. Crystal quality of the films was analyzed by cross-sectional transmission electron microscopy.

Wednesday June 17, 1998
Mercredi 17 juin 1998

Afternoon
Après-midi

SESSION V - Poster Session II : Growth
17:00 - 18:30

- D-V/P1** DOMAIN WALL SPLITTING AND CREATION OF THE FINE DOMAIN STRUCTURE BY ALLOYING IN PZT, D. Fuks, Mater. Eng. Dept., POB 653, BGU, Beer Sheva, Israel; S. Dorfman, Dept. of Phys., Technion, 32000 Haifa, Israel; A. Gordon, Dept. of Math. and Phys., Haifa Uni. at Oranim, 36006 Tivon, Israel
The alloying-induced effect on ferroelectric properties follows from the peculiarities of ferroelectric domains at first-order phase transitions. The profile of the ferroelectric domain wall close to a first-order phase transition is given by a steady-state solution of the Ginzburg-Landau equation of motion. We see that for some concentrations of alloying element in PZT crystals a layer of the paraelectric phase appears. This phenomenon occurring with increasing temperature below T_c is called the wetting of the domain wall by the disordered paraelectric phase. Thus, the alloying-induced wetting of the ferroelectric domain wall at the first-order paraelectric phase transition takes place indicating the splitting domain wall into two interphase boundaries separating between the paraelectric phase and the polarization-up and polarization-down regions. The nucleus of the paraelectric phase appears on the domain wall under the influence of a concentration change.
- D-V/P2** IN-PLANE PARAMETER OSCILLATORY BEHAVIOUR DURING TWO-DIMENSIONAL HETERO-EPI-TAXY OF METALS, S. Andrieu, L. Hennet, M. Alnot, Laboratoire de Physique des Matériaux, UMR7556, CNRS-Université H. Poincaré, 54506 Vandoeuvre, France
In 1993, Massies and Grandjean [1] reported for the first time an oscillatory behaviour of the in-plane parameter during two-dimensional (2D) epitaxial growth of InGaAs on GaAs, as observed by RHEED. Recently, a similar phenomenon was observed in the field of metal epitaxy, in the particular case of Co growth on Cu(001) [2]. This in-plane parameter oscillatory variation is correlated with the RHEED intensity oscillations, and is explained by the partial relaxation of the atomic distance in 2D islands due to the mismatch between the surface lattice and the deposit. We will show that this physical process is often observed in the case of hetero-epitaxy of metals for which a 2D pseudomorphic growth is observed. However, the theoretical explanation of this in-plane distance variation is not satisfactory in some cases. First of all, in the case of square lattice, these in-plane parameter variations are observed to depend on the azimuth chosen for the RHEED observation, whereas an isotropic behaviour is expected. Moreover, in the particular case of V epitaxial growth on (001) Fe, the in-plane parameter is observed to decrease, whereas the bulk V parameter is higher than the Fe one. Different attempts to explain these new results will be discussed.
[1] - J. Massies and N. Grandjean, Phys.Rev.Lett., 71, p1411, (1993)
[2] - J. Fassbender et al, Phys.Rev.Lett., 75, p4476, (1995)
- D-V/P3** PULSED LASER DEPOSITION OF SmBaCuO THIN FILMS, A. Di Trollo and A. Morone, CNR-Istituto per i Materiali Speciali, Area della Ricerca di Potenza, P.O. Box 13, 85050 Tito Scalo (PZ), Italy
The SmBaCuO compound is potentially attractive for developing High Temperature Superconductors (HTS) applications. In this work we deal with the thin films deposition of SmBaCuO by means of Pulsed Laser Ablation. We report the SmBaCuO film properties by changing the relevant fabrication parameters, such as the laser fluency, the substrate temperature and the oxygen gas pressure. Under suitable parameters the film show an epitaxial growth in the the 001 direction on the crystalline MgO (100) substrate. In addition, these films have a sharp superconducting transition in the resistivity vs. temperature behavior at a temperature $T > 77K$.
- D-V/P4** EPITAXIAL ZIRCONIA FILMS ON SAPPHIRE SUBSTRATES, C. Mary, R. Guinebretière, G. Trolliard, B. Soulestin, and A. Dauter, Laboratoire de Matériaux Céramiques et Traitements de Surface, ESA CNRS 6015, ENSCI, 47 Avenue A. Thomas, 87065 Limoges, France
Sol-gel routes to green state processing of ceramics can provide good control in the distribution of a second constituent. An example of this approach is the preparation of zirconia toughened ceramics through the hydrolysis of zirconium alkoxide on the surface of powders. Sintered ceramics made from these coated powders are fine grained and compositionally homogeneous. Moreover, direct crystallization of zirconia precursor onto host grain surface has an influence upon crystallographic relationships and metastable phase stabilization.
In the present work, the epitaxial development of undoped zirconia films produced via the solution precursor route and deposited by dip-coating on (1120) planes of sapphire is characterized. After drying and firing at 600°C, polycrystalline films are made of nanosized randomly oriented tetragonal ZrO₂ grains. Firing at higher temperatures promotes grain growth and islanding, so producing a layer of heteroepitaxial but isolated grains. Two families of single crystalline islands are identified: $\{100\}_{ZrO_2} // (1120)_{\text{sapphire}}$ and $\{111\}_{ZrO_2} // (1120)_{\text{sapphire}}$. In plane growth of flat $\{100\}$ oriented crystalline can be favored by varying thickness and firing conditions of the films. The complete heteroepitaxial orientation of the pseudo single crystalline film and the interface structure are determined through X-ray diffraction experiments (low incidence XRD, ϕ scans, ω -rocking curves) and cross sectional or in plane HRTEM observations.
- D-V/P5** GROWTH AND MAGNETISM OF Co/NiO(111) THIN FILMS, C. Mocuta, A. Barbier, G. Renaud and B. Dieny, CEA-Grenoble, 17 Av. des Martyrs, 38054 Grenoble Cedex 9, France
Our study is aimed at the description of the relation between the magnetic exchange anisotropy and the structure of a model ferro/antiferromagnetic interface.
The in situ Co/NiO(111) growth was studied by Grazing Incidence X-ray Diffraction (GIXD). Recently, we shown that NiO(111) single crystals could be prepared with a quality compatible with GIXD[1]. The experiments were carried out on the SUV diffractometer of the French CRG- IF beamline at the ESRF. The Co layers structure and the growth mode highly depend on the preparation conditions of the NiO(111) single crystal. Variable quantities of FCC, twinned FCC and HCP Co were obtained. The control of the quality of the substrates and of the growth conditions allowed us to obtain Co films (thickness up to 200Å) containing only one stacking.
Magnetic measurements (Kerr effect, VSM, SQUID) on GIXD in situ characterised samples evidence the high correlation between the magnetic properties and the internal structure of the Co layers. We show that an exchange field and a high coercivity field appear for single crystal substrates. We measured the evolution of these two pertinent quantities at different temperatures.
[1] A. Barbier, G. Renaud - Surf.Sci.Lett., L15, 392 (1997)

- D-V/P6** EPITAXIAL GROWTH OF ZnS ON CdS IN CdS/ZnS NANOSTRUCTURES, C. Ricolleau, L. Audinet, M. Gandais, LMCP, Uni. P6 et P7, Case 115, 4 Place Jussieu, 75252 Paris, Cedex 05 and T. Gacoin, LPMC, Ecole Polytechnique, 91128 Palaiseau, France

The quantum-sized semiconductor nanocrystals have raised a new increasing interest in the field of optical physics. Recently, attempts have been made not only to prepare nanocrystals with well-defined structural properties such a chemical composition, crystallography, mean size, morphology, surfaces but also to manipulate the surfaces which may strongly influence the physical properties. One of the methods for controlling the surface consists in the coating of nanocrystals by a shell of different species.

The present contribution concerns the structural properties of CdS/ZnS core/shell-like systems prepared by using colloidal chemistry. The CdS/ZnS core-shell heterostructure has been evidenced by using electron microscopy. The epitaxy of ZnS on CdS, the CdS/ZnS interface and the accommodation mode between the two materials will be presented. Furthermore, it has been shown that the ZnS shell grows with the same structure as the CdS core, which is either in the cubic blende type structure or in the hexagonal wurtzite type structure.

- D-V/P7** CONTROLLING THE INTRALAYER STRUCTURE IN Co/Pt-MULTILAYERS, P. Haibach, J. Köble, M. Huth, and H. Adrian, Inst. f. Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany

The effect of the surface quality of MgO (111) substrates seeded by a 3nm thick Pt-layer on the inter- and intralayer structure of Co/Pt-superlattices was investigated. Pre-growth processing of the MgO showed that intensive polishing using a special H_2O/SiO_2 -suspension prior to growth is mandatory for obtaining long range structural coherence in the films.

The Co/Pt-superlattices were deposited by dc magnetron sputtering both on new and re-polished substrates. As confirmed by x-ray reflectometry and AFM analysis, the substrate treatment has no impact on the surface roughness and the interlayer order, but clearly improves the degree of intralayer order, as shown by superlattice-peak rocking curves. Beside a mosaic crystal-like component of $1-3^\circ$ linewidth, which is common to all samples, the films on the re-polished substrates show an extremely narrow, resolution-limited feature ($\Delta\omega < 0.035^\circ$, $\Delta q < 0.047 \text{ nm}^{-1}$) which arises from long range structural coherence. Four circle x-ray diffraction reveals that the Pt-component of the long range-ordered samples grows as a pure fcc-stacked crystal with three-fold in-plane symmetry, whereas the mosaic films grow as a twinned fcc-crystal with six-fold symmetry. The degree of lateral orientation of the Pt- and the Co-layers is improved by more than 30%. These samples of different intralayer quality are used to investigate the connection between the perpendicular and the in-plane magnetic anisotropy using torque-magnetometry.

- D-V/P8** THE CHEMISORPTION - KINETIC MECHANISM OF THE COATINGS HETEROGENEOUS SYNTHESIS, A.G. Varlamov, Institute of Structural Macrokinetics, RAS, Chernogolovka, Moscow region 142432, Russia

In the present work on the base of kinetic investigation of silicon carbonitride layers CVD synthesis the chemisorption - kinetic mechanism of the coatings heterogeneous synthesis was suggested. The decreasing of the coatings growth rate is conditioned by the accumulation of particles, blocking the active centers, and the decreasing of the unblocked centers number. In the course of time a dynamically chemisorption desorption equilibrium which is characterized by a constant number of the unblocked centers, is established, which causes linear growth of coatings. The S-type dependence precise analysis showed that before the inflection point the initial and stationary deposition rates dependence is a monolayer chemisorption isotherm and is described by Langmuir model. In the range of small pressures the dependencies are straight linear and described by Henry law. The change to homogeneous condensation may be connected with homogeneous nucleation facilitation possibility in the polylayer in comparison with gas-phase nucleation. The synthesis temperature and TMS partial pressure influence on the silicon carbonitride deposition investigations showed that chemisorption and solid deposit formation heterogeneous chemical reaction are the leading (limiting) stages defining the CVD-process kinetics. Some mechanism consequences, confirming its correctness are suggested.

- D-V/P9** GAS-PHASE COMPOSITION ANALYSIS WITH IN-SITU METHOD IN SYSTEM GaAs-Bi-AsCl₃-HCl-H₂-He, V.A. Voronin, S.K. Guba, State University Lviv Polytechnic, Dept. Semiconductors Electronic, Bandera Street Lviv-13, 290646, Ukraine

In the present work with the help of situ optical absorption spectroscopy method the concentration of components for the system GaAs-Bi-AsCl₃-HCl-H₂-He were determined in the source region. The investigation was made in the 220-360 nm region at temperatures from 400°C to 900°C, the Reynolds number having been taken from 0.1 to 2. It was shown that homogeneous and non-homogeneous reactions in the source region had nonequilibrium nature.

On the base of analyzes of absorption spectrum data, recieved by the method of UV-spectroscopy it is shown that in the system GaAs-Bi-AsCl₃-HCl-H₂-He in the temperature range 600-700°C the creation of the saturating gas phase and the deposition of GaAs epitaxial films doped by bismuth. It is suggested to use in one of the channels reactor the Bi-AsCl₃-He system as a source for receiving of the necessary concentrations of BiCl₃ in the gas phase.

These allows to operate the gas phases content during the low temperature growth of epitaxial layers of GaAs doped by bismuth by changing the square of source and H₂-He flows.

- D-V/P10** FABRICATION AND ELECTRICAL PROPERTIES OF SOL-GEL DERIVED (BaSr)TiO₃ THIN FILMS WITH METALLIC LaNiO₃ ELECTRODE, Di Wu*, Aidong Li*, Zhiguo Liu*, **, ChuanZhen Ge*, Peng Lu* and Naiben Ming*, **, *National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R. China; **Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, China

Metallic LaNiO₃ (LNO) films were prepared on LaAlO₃ (LAO) and Si substrates by metalorganic decomposition (MOD) and their application as the bottom electrode for sol-gel derived (BaSr)TiO₃ (BST) thin film. X-ray diffraction, scanning electron microscopy and electrical measurements were used to characterize the multilayer films of BST/LNO/substrates. BST film on LNO-coated LAO exhibited preferred (001)-orientation and smooth surface with fine grains (~50nm). The electrical measurement results on BST films respectively using LNO and stainless steel as the bottom electrodes showed BST/LNO/substrate has higher dielectric constant, lower loss tangent, lower leakage current and higher breakdown field.

- D-V/P11** TWO-DIMENSIONAL AND ZERO-DIMENSIONAL STRUCTURES OF SEMIMAGNETIC SEMICONDUCTORS PREPARED BY PULSED LASER DEPOSITION, A.I. Savchuk, I.D. Stolyarchuk, S.V. Medynskiy, Dept. of Phys. Electronics, University of Chernivtsi, 274012 Chernivtsi, Ukraine; A. Perrone, Dept. of Physics, University of Lecce, National Institute of Matter Physics, 73100 Lecce, Italy and P.I. Nikitin, General Physics Institute, 117942 Moscow, Russia

Technique of pulsed laser deposition has been applied for growth of thin films, multiple quantum well structures and nanocrystals of Cd_xMn_{1-x}Te ($x < 0.43$). The advantages in the use of this technique as compared with other methods for the epitaxial growth of Cd_xMn_{1-x}Te layers have been demonstrated. In case of nanocrystals it was possible to avoid strong oxidation of small particles of semimagnetic semiconductor embedded in SiO₂ matrix.

Characterization of the obtained thin films and nanocrystals was carried out by X-ray diffraction, optical absorption and Faraday rotation investigations. The results on magnetooptical properties suggest of modification of exchange interactions in the investigated low- dimensional structures.

This work is supported by European Commission within INCO-Copernicus Programme (grant No.ERBIC15CT960820).

- D-V/P12** EPITAXIAL GROWTH OF MULTICOMPONENT FILMS AT LASER DEPOSITION: EFFECT OF FILM-SUBSTRATE LATTICE MISMATCH, Y.D.Varlamov, M.R.Predtechensky, O.M.Tukhto, Institute of Thermophysics, av.Lavrentyeva 1, 630090 Novosibirsk, Russia
The conditions of epitaxial growth, structure and properties of multielement metaloxide films on the substrates with different film-substrate structural mismatch have been studied. It has been shown that the result of film-substrate lattice mismatch influence are: - the narrow regions and interdependence of deposition parameters wherein the epitaxial growth of films is realised; - the principle role initial stage of film formation; - the existence of several dominant directions of film growth and as result the moderately large disorientation of film axes; - internal stresses in the films and change of film properties. The HREM study of free-standing films shown that the films consist of the micrometer scale monocrystalline regions connected via small angle boundaries. Increased film thickness increases the magnitude of deformation. At the structural phase transition that is typical for some metaloxides the formation of extended line-mesh defects and cracking films can be take place.
The conditions of film growth has been interpreted in terms of composition and energy of the deposited particles and thermodynamics conditions of film formation. The conception of nucleus film growth in conditions of considerable film-substrate lattice mismatch and the relationship of structure and transport film properties have been discussed.
- D-V/P13** RHEED INVESTIGATION OF LIMITING THICKNESS EPITAXY DURING LOW TEMPERATURE Si-MBE ON (100) SURFACE, A.I.Nikiforov, B.Z.Kanter and O.P.Pchelyakov, Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, Lavrentjeva 13, 630090 Novosibirsk, Russia
In the recent years some attempts of decreasing a substrate temperature (T_s) during Si-MBE were made in order to suppress dopant segregation. The limiting thickness of the epitaxial layer (h_{epi}) during low temperature Si-MBE was found using TEM cross-section. A higher thickness causes the growth of an amorphous film. The present work was aimed at determination *in situ* of h_{epi} using RHEED and at studies of h_{epi} as a function of T_s on Si(100) surface.
In order to find h_{epi} a new technique was suggested. It is based on monitoring of intensity variations of a bulk spot in the RHEED pattern during MBE growth. A maximum is seen in the plot of intensity *versus* deposited film thickness. An increasing intensity is observed with a more roughened surface, while "islands" of amorphous phase that appear on the growing surface are responsible for the decrease in intensity. Thus, the maximum intensity corresponds to the limiting thickness of the epitaxial layer. Further Si deposition results in an increase in amorphous fraction and growth of an amorphous film. The activation energy of the limiting thickness epitaxy is 0.5 eV.
Therefore, the process of low-temperature growth and the surface recovery can be controlled *in situ* by monitoring of variations in intensity of diffraction peaks. To achieve the control, registration of intensity variations of not only bulk spots, but also superstructural ones.
- D-V/P14** THE INFLUENCE OF GROWTH TEMPERATURE ON THE PERIOD OF RHEED OSCILLATIONS DURING MBE OF Si AND Ge ON (111) SURFACE, A.I.Nikiforov, V.A.Markov, V.A.Cherepanov* and O.P.Pchelyakov, Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, Pr. Ac.Lavrentjeva 13, 630090 Novosibirsk, Russia ; *Novosibirsk State University, Russia
Temperature dependence of the oscillation period of an electron specular beam, reflected from the surface of an growing epitaxial film was studied. A decrease in the oscillation period with increase of temperature was shown experimentally for Si and Ge epitaxy on the (111) surface. This phenomenon, observed at the range of transition from the 2D growth mechanism to step-flow one, is the result of the lag of the step edge behind its initial position for a distance equal to the migration length of adatom during growth of a continuous atomic layer. The data obtained allowed the adatom migration length to be determined, and its temperature dependence was used to find the activation energy of formation of two-dimensional islands during the epitaxial growth. The activation energy was 1.05 eV for epitaxy of silicon on Si(111) surface and 1.4 eV for the epitaxy of germanium. The influence of growth temperature on the oscillation period should be taken into account, when the registration of oscillations is used to control the growth parameters and to study processes, proceeding on the surfaces of growth.
- D-V/P15** FORMATION OF INTERFACES AND EPITAXIAL THIN FILMS ON CLEAVAGE SURFACES OF II-VI CRYSTALS IN VARIOUS GASEOUS ATMOSPHERES, P.V. Galiy, I. V. Kurilo*, T. M. Nenchuk, I. O. Rudyi*, Q.I. Vlasenko**, J. M. Stakhira, Physical Department, Lviv State University, 50 Dragomanov str., 290005 Lviv, Ukraine, *Department of Semiconductor Electronics, State University "Lviv Polytechnic", 12 S.Bandera str., 290013 Lviv, Ukraine, **Institute of Semiconductor Physics NAS Ukraine, 45 Prospekt Nauky, 252650 Kyiv, Ukraine
The quality of formed nanolayers and CdHgTe, HgTe epitaxial thin films on CdTe and CdMnTe substrates sufficiently depends on presence of oxygen and carbon containing adsorbates and also technologic impurities on the substrate. The adsorption gas activity of CdTe, HgTe (110) cleavages relatively to N_2 , O_2 , CO_2 , CO and water vapour have been studied by AES and mass spectrometry. The influence of temperature and electron beam irradiation on adsorption have been investigated also. Cleavages were obtained in laboratory atmosphere and in AES spectrometer UHV chamber. Surfaces were exposed to mentioned gases under pressure from 10^{-9} Torr up to atmospheric.
As the result it has been determined, that atomically clean CdTe, HgTe surfaces are adsorptially non active relatively to N_2 and reveal activity to carbon containing gases and oxygen. The last one increases with temperature elevation. The composition of interfacial regions- epitaxial thin film / substrate of HgTe/CdMnTe and CdHgTe/CdTe systems, obtained by UHV cleavage normally to the interface, have been studied.
- D-V/P16** NONSEGREGATING $In_xGa_{1-x}P$ PSEUDOMORPHIC EPILAYERS ON GaAs SUBSTRATES, I.S. Chikichev, Novosibirsk State University, Department of Mathematics and Mechanics, Pirogov Street 2, 630090 Novosibirsk, Russia and S.I. Chikichev, Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, Academician Lavrentiev Avenue 13, 630090 Novosibirsk, Russia
Using recently developed model [1] for the surface segregation in nonhydrostatically strained substitutional solid solutions it is shown that for pseudomorphic $In_xGa_{1-x}P$ epilayers there is a unique composition characterized by the absence of equilibrium surface segregation. This composition is found to be almost temperature-insensitive within the range 700-900 K relevant for epitaxial growth techniques, but is highly orientation-dependent. The nonsegregating composition is calculated to be 0.34, 0.21, 0.25 and 0.20 for GaAs substrates with {100}, {110}, {111} A and {111} B orientations, respectively. We conclude that ubiquitous and annoying effect of surface segregation in multicomponent semiconductor alloys can be completely suppressed (at least thermodynamically) by thoughtful choice of substrate lattice constant and orientation. Present work is supported by RFBR under the grant 97-02-18491.
[1] A.V.Vasev, I.S.Chikichev, S.I.Chikichev. "Surface segregation in pseudomorphic Si_xGe_{1-x} crystals". Proceedings of the 20th Internat. Conf. on Semiconductors (CAS'97), Sinaia, Romania, 7-11 October 1997, Published by IEEE.
- D-V/P17** ELECTRICAL PROPERTIES OF HgCdTe FILMS OBTAINED BY LASER DEPOSITION, I. Virt, Section of Experimental Physics, Pedagogical Institute, Gogol 34, 293-720 Drohobich, Ukraine; G. Wysz, M. Kuzma, Institute of Physics, Higher Pedagogical School, Rejtana 16a, 35-309 Rzeszow, Poland
Films of HgCdTe were prepared on Al_2O_3 , NaCl, CsI substrates by YAG:Nd³⁺ pulse laser deposition in dynamical vacuum. Electric resistance of films is relatively high. It is probable due to the high number of structural defects and decrease of Hg atoms concentration. A quality of films depends considerable on the temperature of substrate and the best films grow at the temperature window of 480-490 K.
The temperature characteristics of conductivity clearly point out an intrinsic and a doping regions. For films obtained in temperatures mentioned above these characteristics are compared to those of target. The annealing of films in Hg vapour not only increases Hg concentration in films but orders the structure as well.

- D-V/P18** THE GROWTH KINETICS OF $\text{Si}_{1-x}\text{Ge}_x$ LAYERS IN GeH_4 -Si MBE, L.K. Orlov, V.A. Tolomasov, A.V. Potapov, Institute for Physics of Microstructures, RAS, GSP-105, 603600 Nizhny Novgorod, Russia
We have realized an option of the GeH_4 -Si MBE to grow $\text{Si}_{1-x}\text{Ge}_x$ layers and $\text{Ge-Si}_{1-x}\text{Ge}_x$ MQWS on silicon substrates. The dependencies of Ge content on the germane pressure, atomic Si flow density and the growth temperature have been experimentally studied. The growth kinetic model of alloy epitaxial layers corresponding to the proposed epitaxy method has been created. The model considers disintegration of silane and germane molecules from chemisorption to formation of Si and Ge adatoms and their embedding in a crystal lattice. We have investigated the stationary and non-stationary growth kinetics of alloy layers. The numerical modeling of the stationary epitaxial process has shown good agreement with the experimental data and has allowed to explain peculiarities on the experimental dependencies. The effective frequency of disintegration of GeH_3 molecules was determined. The study of non-stationary processes has allowed to find the conditions providing minimum interface erosion.
The authors thank the Russian Foundation for Basic Research (RFFI, grant No 96-02-19278) for the rendered financial support.
- D-V/P19** THE GROWTH KINETICS OF $\text{Si}_{1-x}\text{Ge}_x$ LAYERS FROM GeH_4 AND SiH_4 , L.K. Orlov, A.V. Potapov, S.V. Ivin, Institute for Physics of Microstructures, RAS, GSP-105, 603600 Nizhny Novgorod, Russia
In the last decade the chemical vapour deposition from silicon and germanium hydrides at low pressures has been actively used for $\text{Si}_{1-x}\text{Ge}_x$ layer epitaxy. Despite the large number of experimental works the number of theoretical researches is insignificant, and the available models describe experimental data inadequately. In the present paper we offer a model of the growth kinetics of $\text{Si}_{1-x}\text{Ge}_x$ layers from silane and germane molecular flows and discuss the features of growth from both SiH_4 and GeH_4 and in the presence of Si and Ge atomic flows (hot wires method). The model considers disintegration of silane and germane molecules from chemisorption to formation of Si and Ge adatoms and their embedding in a crystal lattice. We have investigated the stationary growth kinetics of alloy layers. The numerical modeling of the epitaxial process has shown good agreement with the experimental data and has allowed to explain peculiarities of the experimental dependencies. The effective frequencies of SiH_3 and GeH_3 disintegration for the considered epitaxial method were determined.
The authors thank the Russian Foundation for Basic Research (RFFI, grant No 96-02-19278) for the rendered financial support.
- D-V/P20** CRYSTAL MICROSTRUCTURE OF PbTe/Si AND $\text{PbTe/SiO}_2/\text{Si}$ THIN FILMS, Y.A. Ugai, A.M. Samoylov, A.V. Tadeev, M.K. Sharov, Voronezh State University, Universitetskaya Sq. 1, 394693 Voronezh, Russia
It is well known that PbTe/Si and $\text{PbTe/SiO}_2/\text{Si}$ thin films are used for marking of the low cost infrared focal plane sensor arrays for thermal imaging or spectroscopic application. Thereby, the investigation of the microstructure is sufficiently important because the real parameters of IR detectors would depend on crystalline quality of these PbTe deposited layers.
The mirror-smooth surface PbTe thin films (thickness was about $0.5\text{-}0.7\mu\text{m}$) were deposited on (100) Si high ohmic substrates both with and without SiO_2 buffer layer by modified "hot wall" technique using the thermal evaporation of the elements from separate sources. The crystal microstructure of PbTe thin films has been studied by etching pits method, SEM, RHEED and by x-ray analysis which is able to determine the x-ray rocking curve profiles and line width with the high precision. The investigation of thin films dislocation density by etching pits method and by the analysis of x-ray reflection profiles show that the average values for PbTe/Si films is about 10^6 cm^{-2} , but for $\text{PbTe/SiO}_2/\text{Si}$ films is $\approx 10^5\text{ cm}^{-2}$. It is necessary to note that $\text{PbTe/SiO}_2/\text{Si}$ heterostructures have been characterized by the average values of dislocation density which were approximately ten times low then the same parameters for PbTe/Si films grown under the identical experimental conditions.
- D-V/P21** ON THE GROWTH OF EPITAXIAL CoSi_2 BY THE SOLID PHASE REACTION OF Co/METAL BILAYERS WITH $\text{Si}(001)$, M. Falke, B. Gebhardt, G. Beddies, S. Teichert, H.-J. Hinneberg, Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
Among the epitaxial transition metal silicides CoSi_2 is of special interest for applications in ULSI technology because of its high thermal stability and low electrical resistivity. The solid phase reaction of metallic bilayers with Si in an N_2 ambient is a well known HV process for growing epitaxial CoSi_2 . But the real function of the so-called diffusion barrier, arising during the annealing process, remains unclear. TEM studies and RBS measurements revealed the intermediate growth of a CoSi phase with grains of preferred orientation to Si. The growth of this phase rises the temperature of CoSi_2 nucleation, which starts at the CoSi/Si interface. This nucleation temperature determines the quality of the growing epitaxial CoSi_2 . It is better for Ti as barrier forming material than for Hf used successfully as well [1]. Whether an intermediate oriented growth of CoSi is promoting the epitaxial quality of CoSi_2 , otherwise than by shifting the nucleation temperature, remains an open question.
[1] B. Gebhardt, M. Falke, G. Beddies, H.-J. Hinneberg, Micro-electronic Engineering 37/38 (1997) 483-490.
- D-V/P22** ATOMIC LAYER EPITAXY OF SiGe:C BY LP(RT) CVD, B. Tillack, E. Bugiel, D. Krüger, R. Kurps, K. Glowatzki, Institute of Semiconductor Physics, Walter-Korsing-Str. 2, 15230 Frankfurt (Oder), Germany
 SiGe:C atomic layer epitaxy has been achieved by Low Pressure (Rapid Thermal) Chemical Vapour Deposition, LP(RT)CVD, using $\text{SiH}_4/\text{GeH}_4/\text{H}_2$ and methylsilane as the source gas for C at temperatures between 200°C and 600°C .
Atomic control of C incorporation has been obtained through surface adsorption equilibrium of methylsilane. C doses below one monolayer have been deposited by separating adsorption of methylsilane and deposition of SiGe . Measurements of the C coverage dependence on the partial pressure of methylsilane show a typical saturation behaviour. The process is self limited. The C coverage increases with temperature. Below 450°C the dominating process is dissociative adsorption of methylsilane without layer growth. The C coverage is below one monolayer. At higher temperatures deposition of Si from methylsilane occurs also creating surface sites for further adsorption of methylsilane. Therefore C coverages higher than one monolayer were estimated. The C dose incorporated into SiGe may be controlled by partial pressure of methylsilane as well as by hydrogen partial pressure. The results indicate atomic control of SiGe:C epitaxy at very low temperature which is essential for instance for the modification of the diffusion properties of the base material of an heterojunction bipolar transistor to prevent the outdiffusion of boron.
- D-V/P23** ATOMIC ORDERING IN $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ DEPOSITED BY MOCVD, K. Cohen, S. Stolyarova, N. Amir, Y. Nemirovsky, Kidron Microelectronics Research Center, Department of Electrical Engineering, Technion - Haifa 32000, Israel. R. Beserman, A. Chack and R. Weil. Solid State Institute, Department of Physics, Technion - Haifa 32000, Israel
For the first time Long Range Order effect was observed in $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ epilayers. Ternary $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ layers were deposited on CdTe (100) substrates by Metalorganic Chemical Vapor Deposition (MOCVD) using a horizontal reactor. The crystalline quality and the morphology of the ternary layers were studied as a function of the growth temperature (T_g), partial pressure ratio (R_{vpr}) and zinc content (x). The valence band splitting was measured by Polarized Photoluminescence, at 77K . This anisotropic property, correlated to Long Range Order (LRO) effect, was similarly observed in III-V atomic ordered materials. The "ordering parameter" η , quantifying the amount of ordered material, was calculated from the valence band splitting. Order has been measured in the temperature range $450^\circ\text{C} < T < 480^\circ\text{C}$ where η varies between $0.5 < \eta < 0.6$.
The atomic ordering was also confirmed by Transmission Electron Microscopy. The ordered phase observed in $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ epilayers have the CuPt -like structure.

- D-V/P24** **HEAVY DOPING CHARACTERISTICS OF P AND B IN $\text{Si}_{1-x}\text{Ge}_x$ EPITAXIAL FILMS**, J. Murota, A. Moriya, M. Sakuraba, T. Matsuura, Res. Inst. of Electr. Comm., Tohoku Univ., Sendai 980-8577, Japan
In-situ heavy doping of P and B in $\text{Si}_{1-x}\text{Ge}_x$ (0.15 < x < 0.85) epitaxial growth at 550°C on the Si(100) substrate with a SiH_4 - GeH_4 -(PH₃ or B₂H₆)-H₂ gas mixture was investigated by using an ultraclean hot-wall LPCVD system. In the case of P doping, in the higher PH₃ partial pressure region than ~1mPa, the deposition rate decreased and the Ge fraction x increased. The P concentration increased up to a maximum value (around $2 \times 10^{20} \text{cm}^{-3}$) and then decreased with increasing PH₃ partial pressure. The electrically inactive P atoms were observed in the higher Ge fraction than 0.5 independently of the P concentration. In the case of B doping, the deposition rate decreased only at the higher GeH₄ partial pressure and the Ge fraction scarcely changed with increasing B₂H₆ partial pressure. The B concentration increased nearly proportionally up to 10^{20}cm^{-3} with increasing B₂H₆ partial pressure, nevertheless these films were single crystals. The carrier concentration was nearly equal to the B concentration up to about $2 \times 10^{20} \text{cm}^{-3}$, and it tended to saturate around $5 \times 10^{20} \text{cm}^{-3}$. By the formulation based on the Langmuir-type adsorption and reaction scheme, these doping characteristics can be explained if it is assumed that the SiH_4 , GeH_4 , PH₃ and B₂H₆ adsorption/reactions and the solid solubility of P and B are different at the Si-Si, Si-Ge and Ge-Ge pair sites on the surface, and that the reactant gas adsorption/reactions are inhibited at the dopant adsorbed sites.
- D-V/P25** **DYNAMICS OF INTERDIFFUSION IN STRAINED Si/Ge SUPERLATTICES OF NANOMETER PERIODS**, Yu. L. Khait, R. Beserman, W. Freiman, Solid State Institute, Technion, Haifa, Israel and K. Dettmer, Institute of Semiconductor Physics, T.U. Braunschweig, Germany
We consider an application of the electron affected dynamics [1] of atomic interdiffusion in Si/Ge strained superlattices (SLS) of nanometer periods, which have been studied by Raman scattering technique. The measured intermixing time intervals t_i and the diffusivities D follow the Arrhenius equation with the activation energy DE and the preexponential factor D_0 dependent on the SLS thickness and strain. In symmetric Si12Ge12 and non symmetric Si19Ge9 SLS, $DE = 1.78 \pm 0.15 \text{ eV}$ and $3.94 \pm 0.15 \text{ eV}$ respectively and $D_0 = 2.10 \cdot 10 \text{ cm}^2/\text{s}$ and $0.7 \text{ cm}^2/\text{s}$ respectively [2]. Explanation of the observed phenomena are proposed in terms of the electron-affected dynamics of atom diffusion and related processes in solids [1,2,3], the agreement between experiment and theory is good. The observed processes consist in a great number of nanometer picosecond electron-affected atomic diffusion jumps over the energy barriers. Each of these events is generated by short lived (picosecond) large energy fluctuations (SLEF) of some atoms and the strong electron-lattice interaction generated by SLEF, which can affect strongly the diffusion parameters [1,2,3].
[1] Yu.L. Khait, Kinetics and applications of atomic diffusion in solids: Nanoscopic electron-affected stochastic dynamics (SCITEC, Switzerland, 1997).
[2] K.Dettmer, W.Freiman, M.Levy, Yu.L.Khait and R.Beserman; Appl. Phys. Lett. 66, 2376 (1995).
[3] W.Freiman, R.Beserman, Yu.L. Khait, M.Shaanan, K.Dettmer, and K.Kessler; Phys. Rev. B48, 2282 (1993).
- D-V/P26** **DIFFUSION OF Cd, Mg AND S IN ZnSe-BASED QUANTUM WELL STRUCTURES**, M. Kuttler, M. Straßburg, U. W. Pohl, D. Bimberg, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
The knowledge of self-diffusion of lattice constituents in quantum well structures is of basic importance for device fabrication. We studied the diffusive properties of Cd, Mg and S in ZnSe-based superlattice structures by annealing the samples in various atmospheres and characterizing them by SIMS and X-ray diffraction. Distinct differences were found in the diffusion of group II and group VI elements. ZnCdSe structures were stable under Zn atmosphere at temperatures well above 500°C, while complete intermixing is observed at 430°C in Se ambient. The diffusion coefficient of Cd turns out to be governed by the generation of column II vacancies and is enhanced by 3 orders of magnitude in p-type material. Similar observations were made for Mg in ZnMgSSe/ZnSSe leading to the conclusion that both group II elements diffuse via column II vacancies. ZnSSe/ZnSe structures turn out to be stable up to 530 °C under Se atmosphere and 750 °C under Zn ambient. In contrast to the results obtained with group II elements, the diffusion of group VI elements can be explained in terms of interstitial diffusion combined with kick-out processes inducing the observed intermixing.
- D-V/P27** **EPITAXIAL GROWTH OF ZnS ON CdS IN CdS/ZnS NANOSTRUCTURES**, C. Ricolleau, L. Audinet, M. Gandais, LMCP, Univ. P6 et P7, Case 115, 4 place Jussieu, 75252 Paris Cedex 05 and T. Gacoin, LPMC, Ecole Polytechnique, 91128 Palaiseau, France
The quantum-sized semiconductor nanocrystals have raised a new increasing interest in the field of optical physics. Recently, attempts have been made not only to prepare nanocrystals with well-defined structural properties such a chemical composition, crystallography, mean size, morphology, surfaces but also to manipulate the surfaces which may strongly influence the physical properties. One of the methods for controlling the surface consists in the coating of nanocrystals by a shell of different species. The present contribution concerns the structural properties of CdS/ZnS core/shell-like systems prepared by using colloidal chemistry. The CdS/ZnS core-shell heterostructure has been evidenced by using electron microscopy. The epitaxy of ZnS on CdS, the CdS/ZnS interface and the accommodation mode between the two materials will be presented. Furthermore, it has been shown that the ZnS shell grows with the same structure as the CdS core, which is either in the cubic blende type structure or in the hexagonal wurtzite type structure.
- D-V/P28** **CORRELATION BETWEEN THE SIGN OF STRAIN AND THE SURFACE MORPHOLOGY AND DEFECT STRUCTURE OF InAlAs GROWN ON VICINAL (111)B InP**, A. Georgakilas, K. Harteros, K. Tsagaraki, Z. Hatzopoulos, Univ. Crete and FORTH, Iraklion, Greece; A. Villa, N. Becourt, F. Peiro, A. Cornet, Univ. Barcelona, Barcelona, Spain; N. Chrysanthakopoulos and M. Calamitoutou, Univ. Athens, Athens, Greece
We have investigated the MBE growth of InAlAs layers and InGaAs/InAlAs heterostructures on vicinal (111)B InP substrates, misoriented by 1° toward [-211]. We used SEM and AFM for surface morphology observations, TEM for crystal defect analysis and High Resolution XRD for strain evaluation. A dependence of InAlAs surface morphology on the layers' strain type was observed; tensile strained InAlAs layers exhibited smooth surfaces, often with depressions, while compressively strained layers showed a periodical structure of large bunched steps. Twins and other defects were observed in the tensile layers but only threading dislocations in the compressive layers. The spacing between bunched steps increased monotonically with epilayer thickness in the region of 0.3-1.2 micrometers. Our results indicate the significant influence of the sign of strain in the strain relaxation and adatom surface diffusion processes.
- D-V/P29** **ALLOTAXY IN THE SYSTEM Ni-Si**, S. Teichert, M. Falke, H. Giesler, G. Beddies and H.-J. Hinneberg, Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
The allotaxy developed by S. Mantl and H. Bay is a special method to grow heterostructures. In the first process step precipitates of the material B or of the compound AB₂ grow in a matrix A accomplished by codeposition of A and B. In the following step of thermal annealing the precipitates can be transformed by Ostwald-ripening into a buried film being epitaxial or not in dependence on its structure. The quality of the resulting epitaxial film is mainly determined by the size and distribution of the precipitates. In the first process step of allotaxy a couple of process parameters can be tuned in order to get the desired precipitate distribution. But there are also given material parameters with a strong influence, especially the product of the diffusion coefficient and solid solubility of B in A has a great impact on the result of allotaxy. For the group of 3d metals forming interesting silicide compounds in the silicon matrix this product has the highest value for Ni. Therefore the Ni-Si system is a borderline case in respect to allotaxy revealing its limitations. In this work we investigate the influence of allotaxy temperature, deposition rates and Ni-profile on the size and distribution of precipitates in the Ni-Si system. The preparation of the samples was performed under UHV conditions by electron beam evaporation. All samples were analyzed by random and aligned He backscattering spectra. Cross-section TEM gives additional information on the crystalline structure of the prepared samples.

SYMPOSIUM D

- D-V/P30** ION BEAM DEPOSITION OF NANOCRYSTALLINE AND EPITAXIAL SILICON FILMS, H.R. Khan, FEM, Material Physics Department, Schwaebisch Gmuend, Germany and H. Frey, Loet und Schweißgeraete GmbH, 73773 Aichwald, Germany
Deposition of Nanocrystalline and epitaxial silicon films and investigation of the growth mechanism and physical properties are important, because of their use in microelectronics. Silicon films of various thicknesses were deposited on glass (amorphous) and Si(<111>-orientation) substrates at various temperatures using an R.F. ion beam source and SiH₄ and SiH₄+H₂ plasmas. The Si⁺ ions of various energies were extracted from the plasma and deposited on the substrates. The films deposited with ions of energies larger than 20 eV were nanocrystalline with preferred crystallographic orientations whereas the films with lower energies deposited on Si<111> substrates at 500°C showed an epitaxial growth. The nanocrystallinity and epitaxial growth as well as microdeformation in the films investigated by X-ray diffraction techniques as a function of the deposition parameters will be reported.
H.R. Khan, H. Frey and F. Banhart; Nuclear Instruments and Methods in Physics Research B 112 (1996) 289-293
- D-V/P31** FORMATION AND STABILITY OF ERBIUM-SILICIDE GROWN EPITAXIALLY ONTO Si(100)2x1 SURFACE, G. Peto, G.L. Molnar, I. Eördögh, Z.E. Horvath, E. Zsoldos, J. Gyulai, MTA Research Institute for Technical Physics and Materials Science, 1525 Budapest, PO Box 49, Hungary
1-6 nm thick Er film was evaporated by e-gun onto Si(100) 2x1 surface in UHV and annealed in-situ to form silicide by solid phase reaction. The growth was monitored by RHEED using 10keV energy with image analysis. The as-evaporated Er film was polycrystalline, but the 700°C annealing for 3 min induced sharp good quality streak pattern. Further annealing at 900°C for 20 min produced gradually a spot like pattern instead of the streaks. Er-silicide samples were measured ex-situ by X-ray diffraction, transmission electron microscopy (TEM), and Rutherford Backscattering. Annealing at lower temperature (700°C) induces epitaxial ErSi₂ film onto Si(100). The higher annealing induced the Er-silicide/silicon system changing to textured polycrystalline ErSi₂, moreover XTEM investigation showed ErSi₂ islands. This observation may be explained by a Stransky-Krastanov type transformation because of the lattice mismatch between the film and substrate. The other explanation would be a structural change in Er-silicide compound to Er-silicon dilute alloy. This process is in conflict with bulk thermodynamical data of the Er-Si system. One may suggest a thickness dependent transition which may be supported by the fact that the above silicide deterioration is enhanced for thinner layers of Er.
- D-V/P32** INFLUENCE OF GROWN - IN DEFECTS ON THE OPTICAL AND ELECTRICAL PROPERTIES OF Si/Si_{1-x}Ge_x/Si HETEROSTRUCTURES, R. Loo, M. Caymax, E. Simoen, D. Howard*, IMEC, Kapeldreef 75, 3001 Leuven, Belgium; *present address: Rockwell Semiconductor Systems, Newport Beach, CA 92660-3095, USA; M. Goryll, D. Klaes, L. Vescan, ISI-Research Centre Jülich GmbH, 52325 Jülich, Germany; D. Graveteijn, Philips Research Laboratories, P.O. Box 80000, 5500 JA Eindhoven, The Netherlands; H. Pettersson, Department of Solid State Physics, Lund University, P.O. Box 118, 22100 Lund, Sweden
Si and Si_{1-x}Ge_x CVD Epitaxial layers were grown at reduced pressure in a production ASM Epsilon-One reactor. Both undoped and modulation doped Si/Si_{1-x}Ge_x/Si heterostructures, grown at 700°C, show sharp and intense SiGe photoluminescence with a FWHM of 6.5meV for the no phonon lines. Growth at 625 or 575°C caused the intensity of the SiGe luminescence to decrease, but the intensity is recovered after annealing the samples in a H₂-plasma at 400°C for 30min. In these layers, oxygen and carbon were found to be below the SIMS detection limits, indicating that non-radiative recombination centres are grown-in during epitaxial growth at low temperature. DLTS showed the presence of a deep level of defects (525meV above the valence band maximum) in one sample. The influence of growth parameters (temperature and layer growth sequence) on the optical and electrical properties was investigated using modulation doped samples. At 4K, hole mobilities up to 8616cm²/Vs and hole concentrations of 6.5x 10¹⁶cm⁻³ were measured.
- D-V/P33** LOW TEMPERATURE EPITAXIAL GROWTH OF Si ON Si (111) BY-GAS-SOURCE MBE WITH CYCLIC THERMAL ANNEALING, Takashi Ishikawa, Hiroshi Okumura, Toshimitsu Akane, Masashi Sano, Satoru Matsumoto, Dept. of Elec. Eng., Keio Univ., Hiyoshi Yokohama 223, Japan
Low temperature growth technique of Si on Si(111) for gas-source molecular beam epitaxy(LT-GS-MBE) has been proposed. This technique uses cyclic thermal annealing (CTA) to improve defective crystallinity of the film obtained at low growth temperature (525°C). Tapping-mode atomic force microscope was used to investigate the surface morphology. In this study, we did not define times as the intervals but film thickness grown between annealings.
Dependence of annealing temperature and the interval on surface morphology has been investigated in detail. Annealing temperature of 750°C makes the 3D-surface grown at 525°C flat if the interval is fixed at 7nm. The influence of the interval on the surface morphology vanishes in the case where the interval is fixed larger than 7nm. Once atomic-steps are formed, further annealing has little influence on the terrace width. Repetition of LT-GS-MBE cycle gives rise to little change in the surface morphology.
It is found that CTA is effective both for flattening the surface and for lowering thermal budget under proper CTA condition.
- D-V/P34** STRONG SURFACE SEGREGATION OF Sb ATOMS AT LOW TEMPERATURES DURING Si MOLECULAR BEAM EPITAXY, Z.M. Jiang, C.W. Pei, L.S. Liao, J. Qin and Xun Wang, Surface Physics Laboratory, Fudan University, Shanghai 200433, China; Q.J. Jia, X.M. Jiang, BSRF, Ins. High Energy Phys., China; Z.H. Mao, I.K. Sou, Dept. of Phys., USTHK, UK
Surface segregation of Sb atoms at temperature below 400°C during Si molecular beam epitaxy growth are studied by ex-situ X-ray reflectivity measurements and secondary ion mass spectroscopy (SIMS). The samples were grown with a molecular beam epitaxy system Riber EVA-32. One monolayer of Sb atoms were first deposited at the temperature of 500°C, followed by a 23nm thick Si overlayer grown at different temperatures of 250, 300, 350, and 400°C. The decay lengths of dopant Sb distribution profile are obtained to be 0.45, 0.95, 3.5, and >30nm by the simulations of their X-ray reflectivity curves, respectively. A strong surface segregation of Sb atoms is observed at temperatures of 350 and 400°C, which is also confirmed by the SIMS profiles, however it is not consistent with the theoretical prediction that the surface segregation of Sb atoms is totally kinetically limited at the temperatures below 400°C.
- D-V/P35** HETEROSTRUCTURES ZnSe-PbS: BASIS FOR NEW DEVICE CONCEPT, G. Khlyap, M. Andrukhiy, Pedagogical Institute, 24 Franko str., Drogobych 293720, Ukraine
Heterostructures n-ZnSe-n-PbS and n-ZnSe-p-PbS were grown by low-temperature (T~540 K) MBE technology of lead sulphide thin films (d=1 ÷ 3µm) on monocrystalline (110) orientation ZnSe substrates. Structural and electrical measurements have been shown following results: PbS films are of tessellated surface structure with tessell element size of 0.01 ÷ 0.1µm; current transport is realized not only through the space charge region on the heterointerface but along the so-called tunneling channels appeared on PbS film surface due the peculiarities of its structure. This phenomena indicates on formation of p-n and n⁺-n heterojunctions circuits without additional technological methods for device construction.

D-V/P36

EPITAXIAL GROWTH OF Fe/Tb AND Tb/Fe BILAYERS ON Nb(110)/Al₂O₃(11-20), F. Richomme, T. Ruckert*, W. Keune*, J. Teillet, Laboratoire de Magnétisme et Applications, UMR 6634, Faculté des Sciences de Rouen, 76821 Mont-Saint-Aignan Cedex, France, *Laboratorium für Angewandte Physik, Gerhard-Mercator Universität Duisburg, 47048 Duisburg, Germany.

Amorphous and polycrystalline RE/TM multilayers are extensively studied because of their perpendicular magnetic anisotropy (PMA). The interfaces of polycrystalline Tb/Fe multilayers were found to contain strongly disordered Tb-Fe regions which might be responsible for PMA. The question whether sharp hcp-Tb/bcc-Fe interfaces induces PMA is still open. We studied the epitaxial growth of Fe/Tb and Tb/Fe bilayers in order to answer this question. The epitaxial growth of individual Fe(110) and Tb(0001) films on Nb(110)/Al₂O₃(11-20) in MBE system was obtained successfully. Also, epitaxial bilayers of Fe(110)/Tb(0001) and Tb(0001)/Fe(110) on Nb(110)/Al₂O₃(11-20) were grown successfully. LEED patterns indicate a high crystalline quality. The composition and the cleanliness of the surface were systematically checked by Auger spectroscopy. The optimized conditions of epitaxy were determined performing the investigations as a function of the temperature of deposition and the layer thicknesses. We observed Nishiyama-Wassermann or Kurdjumov-Sachs orientation for Fe on Tb and Tb on Nb, depending on the growth conditions. The deduced in-plane relationships were found reproducible. Ex-situ X-ray diffraction was used to determine the epitaxial orientation perpendicular to the plane and the film morphology. The nanostructure of the epitaxial films will be correlated with the structural and magnetic state of the Fe layers given by Mössbauer spectrometry and the spins configurations deduced from polarized neutrons reflectometry measurements. This work is supported by Deutsche Forschungsgemeinschaft (SFB 166).

Friday, June 19, 1998
Vendredi 19 Juin 1998

Afternoon
Après-midi

SESSION IX - Poster Session III: Analysis
14:10 - 15:30

- D-IX/P1** DETERMINATION OF LIGHT AMPLIFICATION PROCESSES IN MOCVD GROWN ZNCDS GRINSCH STRUCTURES, I. Mikulskas, D. Brinkmann*, K. Luterova**, R. Tomasiunas, B. Hönerlage*, J.V. Vaitkus, R.L. Aulombard***, and T. Cloitre***, Institute of Materials Science and Applied Research, Vilnius University, Sauletekio 10, 2040 Vilnius, Lithuania, *Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe d'Optique Non Linéaire et d'Optoélectronique, UMR 46 CNRS-ULP-ECPM, 23, rue du Loess, B.P. 20 CR, 67037 Strasbourg Cedex, **Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 16200 Praha, Czech Republic, ***Groupe d'Etudes des Semiconducteurs, Case Courrier 074, Université de Montpellier II, place Eugene Bataillon, 34095 Montpellier Cedex 05, France
We present results concerning the light amplification in optically pumped ZnCdSe GRINSCH (Graded Refraction Index Separate Confinement Heterostructures). At low temperatures, the spectrally resolved variable stripe length technique was applied for our investigations. In several MOCVD grown, differently designed samples we observe the presence of two gain mechanisms, which involve localized excitons and exciton-exciton inelastic scattering processes, respectively.
New information concerning gain enhancement due to improved light guiding properties of GRINSCH is presented. When simulating the experimental results theoretically, the total gain of the structure has been analyzed. We show that it can be optimized with respect to efficient lasing and threshold lowering. On the basis of our result we also discuss the advantages of GRINSCH over single quantum well design in blue-green laser fabrication.
- D-IX/P2** CdS/InP POLARIMETRIC PHOTODETECTORS, V. Yu. Rud', State Technical University, 29 Polytekhnicheskaya st., 195251 St. Petersburg, Russia and V.M. Botnaryuk, State University, Kishinev, Moldova
Cadmium sulfide and indium phosphide based heterostructures heretofore have been studied only for the purpose of creating high-efficiency solar cells. In the present paper we report the initial results of an experimental study of the photoelectric properties of CdS/InP devices in linearly polarized light (LPL) that have allowed us to draw conclusions regarding their new applications.
The n-CdS/p-p-InP structures formed by the epitaxial growth of cadmium sulphide and indium phosphide films on p-InP substrates with (100) crystallographic orientation. These structures exhibit a photosensitivity approximately 0.13 A/W in the spectral range from 1.3 to 2.4 eV at room temperature. Polarization photosensitivity was observed only for oblique incidence of LPL on the CdS surface of these devices. The induced photopleochroism of these structures was governed by the angle of incidence Θ . The photopleochroism coefficient increase proportionally to Θ^2 and its maximum value is found to be around 50% at $\Theta \approx 75^\circ - 80^\circ$ deg. The maximum azimuthal photosensitivity of CdS/InP heterostructures reaches 0.13 A/W*deg at room temperatures, that is at the record level of this parameter for semiconductor polarimetric photodetectors.
- D-IX/P3** ADATOM DIFFUSION ON 3C-SiC(111) SURFACES, D. Stock, Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Max-Wien-Platz 1, 07743 Jena, Germany
Due to its unique physical properties silicon carbide is considered to be the material of choice for the use in electronic devices operating under extreme conditions, e.g. at high temperatures. With respect to industrial applications the controlled growth of SiC polytypes is challenging. Therefore, an atomistic level understanding of the growth process that mainly occurs on the hexagonal Si-C bilayer is of fundamental interest. By means of large-scale molecular dynamics simulations based on a classical bond-order potential we investigate the dynamics of adatom diffusion on Si-terminated 3C-SiC(111) surfaces. In particular, we characterize the adsorption sites, identify the migration paths, and calculate the diffusion coefficients for Si and C adatoms as well. A comparison with results from first-principles calculations will be given. Furthermore, the dynamics of different Si adatom coverages and the behaviour of deposited C atoms are studied. As will be discussed, the performed simulations provide physical insight into the initial stages of SiC growth by molecular beam epitaxy.
- D-IX/P4** HOLE MOBILITIES IN PSEUDOMORPHIC $\text{Si}_{1-x}\text{Ge}_x$ ALLOY LAYERS, R. Duschl, H. Seeberger and K. Eberl, Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany
Transport properties of Boron doped tensile strained, perfectly strain compensated and compressively strained $\text{Si}_{1-x}\text{Ge}_x$ alloy layers on Si(001) substrates are presented. Hall measurements show the reduction of hole density by adding small amounts of C (<1%) under identical growth conditions and dopant fluxes. This effect is measured over a large temperature range between 50 K and 300 K and is almost independent of the Ge content. The room temperature mobility decreases with C and Ge alloy concentration compared to pure Si from 180 cm^2/Vs ($p=3 \cdot 10^{17}/\text{cm}^3$) to 120 cm^2/Vs , which is explained by the increasing alloy scattering. At temperatures below 100 K a higher mobility up to 6000 cm^2/Vs ($p=1 \cdot 10^{14}/\text{cm}^3$) at 50 K is measured for the samples containing C due to the lower carrier concentration, and because ionized impurity scattering becomes dominant. In modulation doped p-type $\text{Si}_{1-x}\text{Ge}_x$ quantum wells we observe an increased hole mobility with C alloying compared to reference samples without C. This is a consequence of reduced strain and C induced decreased hole concentration in the quantum well.
- D-IX/P5** CHARACTERISATION OF MODULATION DOPED QUANTUM WELL STRUCTURES GROWN BY RF MAGNETRON SPUTTER EPITAXY, T. Graf, B. Vögeli, H. von Känel, Laboratory for Solid State Physics, HPF F15, 8093 Zürich, Switzerland; J. Stangl, G. Bauer, Johannes Kepler Universität Linz, Inst. for Semiconductor Physics, Altenbergstr. 69, 4040 Linz, Austria; J. Schulze, I. Eisele, Universität der Bundeswehr München, Werner Heisenberg Weg 39, 85579 Neubiberg, Germany
A set of modulation doped quantum well structures has been grown by means of rf magnetron sputter epitaxy (MSE). Although low temperature mobilities determined to date are still far below those observed in samples grown with established techniques [1], our samples do show Shubnikov-de Haas oscillations in ρ_{xx} and flat quantum Hall plateaus in ρ_{xy} . A thorough analysis of the compositionally graded $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(001)$ buffers was made previously with a scanning tunneling microscope (STM). Defect etching revealed a defect density on the order of $2 \times 10^{10}/\text{cm}^2$ for the graded buffers and therefore established the high quality of our virtual substrates. The samples were moreover characterised by high resolution reciprocal lattice mapping (HRRLM) and strain profiles were calculated. The results indicate the minimum buffer thickness necessary for a sufficient strain relaxation in the constant composition part of the buffer.
[1] P. Sutter, D. Groten, E. Müller, M. Lenz and H. von Känel, Appl. Phys. Lett. 67, 3954 (1995)

Tantalum oxide film has recently been extensively studied due to its potential electronic and optoelectronic applications in the semiconductor industry. It is a promising candidate as a capacitor insulator in high density dynamic memories (DRAMs) and in ultra-large-scale-integrated devices due to its high dielectric constant (about 25). Tantalum pentoxide films have been deposited by various methods, such as evaporation, sputtering, oxidation of tantalum, pulsed laser deposition, and chemical vapour deposition (CVD), including thermal CVD, plasma-enhanced CVD and photo-induced CVD. Among these, photo-CVD has received much attention since it is a low temperature process does not subject damage on the processed surface.

In this paper we report the growth of thin tantalum pentoxide films by photo-induced CVD using a xenon excimer lamp on Si (100) and quartz substrates, which are shown by SEM to be homogeneous on a nanometer scale. The effects of irradiation time, gas pressure and substrate temperature on the film formed have been studied using Ellipsometry, Fourier transform infrared spectroscopy and UV spectrophotometer measurements. The FTIR spectra show that low temperature (400°C) annealing under VUV irradiation can remove any suboxides present in the as-deposited films. This totally photon-based approach offers significant potential for low temperature thin dielectric film preparation applied to memory technologies.

D-IX/P7

In an approach of low transparency of barriers tunneling of electrons through a double barrier system with an account of their Coulomb interaction in an interbarrier space (quantum well) has been considered. The quantum state of the well is supposed N-fold degenerated. It was shown that the dependence of quantum well occupation and tunneling current on applied bias has a step-like character at low temperatures and in a region of small applied bias there is a threshold value. These properties are explained by splitting of states in the well due to electron interaction. The considered system also shows bistability properties when the electrons occupy upper levels in the well while lower levels remain empty. Such tunneling state is possible because the tunneling system is unequilibrium but stable. The charge fluctuations in the quantum well and possible applications of the considered phenomena for electronic devices of molecular sizes are discussed.

D-IX/P8

Stuttgart and H. Kibbel, B. Jorke, Daimler Benz Research Center, Ulm, Germany) Epitaxially grown p-i-n junctions with 5-15 nm intrinsic layer-thickness were processed to diodes by mesa etching and contacted by a Cr/Au metallization. Rim currents which often plague mesa devices were reduced by a special design with the contact area separated from mesa rim. The dependence of current voltage characteristics on contact area, on temperature and on external load was investigated. Four different regimes were identified where Zener tunneling, Esaki tunneling, tunneling through midgap states and diffusion of minority carriers dominate the current, respectively. Esaki tunneling leads to a negative differential resistance which causes oscillations depending on the external load. The results are interpreted by considering the nominal intrinsic width, the extension of the depletion layer and the abruptness doping transition.

D-IX/P9

M. Bauer, Institut für Halbleitertechnik, Universität Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany

The reflectance of films was measured ex-situ with a commercial measuring system (NanoSpec). This system measures relative to a measurement standard wafer (Silicon-wafer) over wavelength range from 370nm to 800nm. The reflection graphs have maxima in the range from 410nm to 590nm depending on the Ge-content.

Results obtained by these measurements with NanoSpec measuring system were in a good agreement with SIMS -analysis and XRD data.

D-IX/P10

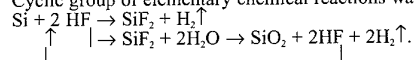
ELECTRON MICROSCOPY METHODS, N.D. Chitcherbaichev, Moscow State Institute of Steel and Alloys, Moscow, O.A. Mironov*, P.J. Phillips, E.H.C. Parker, University of Warwick, UK and A. Romano-Rodriguez, A. Perez-Rodriguez, I.R. Morante, Universitat de Barcelona, Spain, (*also IRE NAS of Ukraine, Kharkiv, Ukraine)

Rodriguez, J.R. Morante, Universitat de Barcelona, Spain, (also IRE NAS of Ukraine, Kharkiv, Ukraine). The exact structural parameters (layers thicknesses and interface roughness) for the 16-period ($\text{Si}_{1-x}\text{Ge}_x$) superlattice grown by solid source MBE in VG Semicron V90S UHV system on (001)Si substrate were determined by high-resolution X-ray diffraction (HRXRD), X-ray reflectivity (XRR), TEM and HREM. The results were compared to data previously obtained by ultra-low energy SIMS. The differences in layer thickness obtained from HRXRD and XRR data are explained by a significant roughening of both Si-on-Ge and Ge-on-Si interfaces. The n and m were determined by the X-ray diffraction methods to be equal to 12 and 4 correspondingly.

D-IX/P11

The process of deepening pores has been examined in silicon by Monte-Carlo method. The silicon sample has porous surface relief making by preliminary anodization with nonhomogeneous tension of electric field. Reetching by water of the silicon samples leads to formation of nano-structures objects system.

Cyclic group of elementary chemical reactions was considered to ensure this process.



For simulation of this process the system of parallel pores is given presenting narrow channels with middle diameter and depth in some atomic layers which arranged normally to surface. Then by Monte-Carlo method the running of reaction is studied. The result of this reaction is deepening of pores. The constant of reaction rate depends from local tension of electric field, which changes by decreasing of surface barrier and according increasing of the holes transport. In consequence of these reasons in places where tension of field is maximum (on the tips of the pores) the accelerating of reaction is happened. The possibility of reaction running in surface or in electrolyte is determined.

Undersaturations, equilibrium constants and exit of reactions are estimated. The information of composition and sample structure is got.

[1] M.E.Kompan, I.Yu.Shabanov. Phys. and Techn. Semicond., **29**, 1859(1995).

- D-IX/P12** THE OSCILLATORIC SECOND HARMONIC DEPENDENCE OF THE DC ELECTRIC FIELD FROM THE Si-SiO₂ MULTIPLE QUANTUM WELLS, A.N. Rubtsov, V.V. Savkin, Department of Physics, Moscow State University, Moscow 119899, Russia

Oscillations of the optical second harmonic the amplitude of the dc-electric field applied to the amorphous Si-SiO₂ multiple quantum wells were observed in experiment. We perform the theoretical study of this effect. We solve the electrostatic part of the problem assuming that current is not flowing through the structure. We suppose that the structure consists of 40 2D rectangular wells (each have two quantized levels in valence and two levels in conductive band) and dielectric layers between them. However, it is assumed that electrons come in wells due to the tunnel effect. The electrostatic interaction between layers is described by Poisson equation. The screening in the single well is described using Hartree approach for each level. The solution is the dependence of the dc potential on the number of layer. This solution at room temperature is monotonic or oscillatoric depending on the thickness of Si and SiO₂ layers. The solution is always monotonic, if the bias voltage is lying within the band gap of Si. Since the second harmonic generation is directly related with the internal dc-field, these oscillations take the place in the second harmonic generation intensity.

- D-IX/P13** ON THE DETERMINATION OF ϵ_{14} IN (111)B-GROWN (In,Ga)As/GaAs STAINED LAYERS, Ph. Ballet, P. Disseix, J. Leymarie, A. Vasson, A.-M. Vasson, LASMEA, UMR 6602 du CNRS, 63177 Aubière, France and R. Grey, Department of Electrical and Electronic Engineering, The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

The growth of semiconducting strained layers on non (100) planes enables novel optoelectronic devices based on internal piezoelectric field effects to be developed. For this purpose, the influence of indium surface segregation and temperature on the determination of the piezoelectric constant ϵ_{14} in In_{0.15}Ga_{0.85}As/GaAs multiple quantum well p-i-n diodes grown by molecular beam epitaxy on (111)B GaAs substrates is investigated. Modulation spectroscopy experiments for different bias voltages applied to the structures are performed together with thermally detected optical absorption experiments. The energy shift of fundamental and excited excitonic transitions is analysed within a model including excitonic effects in order to deduce the value in the (In, Ga)As strained quantum wells. Changes in the bandgap alignment due to the progressive incorporation of indium atoms during the growth are evaluated by using both kinetic and thermodynamical equilibrium models. By considering the In segregation and the effects of temperature, it is possible to derive an experimental value of the piezoelectric constant close to that deduced from the InAs and GaAs binary compounds by the Vegard's law.

- D-IX/P14** PHOTOLUMINESCENCE STUDIES OF As-P EXCHANGE IN GaAs/GaInP₂ QUANTUM WELLS GROWN BY CHEMICAL BEAM EPITAXY, A. Aurand, J. Leymarie, A. Vasson, A.-M. Vasson, LASMEA, UMR 6602 du CNRS, 63177 Aubière, France and M. Mesrine, C. Deparis, M. Leroux, CRHEA-CNRS, Rue Bernard Gregory, Parc Sophia Antipolis, 06560 Valbonne, France

Group V elements exchange during the growth of GaAs/Ga_{0.5}In_{0.5}P quantum wells (QW's) by chemical beam epitaxy is investigated by photoluminescence (PL) experiments as a function of temperature from 4K to 300K. In order to study the As-P exchange at the first interface of the GaAs QW, the GaInP₂ surface is exposed to an AsH₃ flow during various times. At low temperature, PL emission energy doesn't reflect the energy of the fundamental E₁HH₁ excitonic transition due to the Stokes shift between the absorption and the emission.

The QW free exciton energy is then deduced at 4K by fitting the temperature dependence of the photoluminescence energy with the classical expression $E(T) = E_0 - a[1 + 2/\{\exp(\theta/T) - 1\}]$.

The calculation of the E₁HH₁ energies are carried out by taking into account the following phenomena which affect the QW structure: indium segregation, As-P exchange and As and P residual incorporation. The electronic properties of the (Ga,In)(As,P) layers entering now in the QW composition are evaluated from the properties of the ternary alloys. Excitonic binding energies are also evaluated in order to adjust the results of calculations to the experimental values. It is found that As-P exchange rate decreases with the increase of the AsH₃ exposure time.

- D-IX/P15** CHARACTERISATION OF INHOMOGENEOUS FILMS BY MULTIPLE-ANGLE ELLIPSOMETRY, S. Colard and M. Mihailovic, LASMEA, UMR 6602 CNRS, Université Blaise Pascal de Clermont-Ferrand, Les Cézeaux, 24 avenue des Landais, 63177 Aubière Cedex, France

High performance devices often require good quality layers, homogeneous composition and crystallinity, then the homogeneity in depth of the layers is of major interest. This control is usually done by spectroscopic ellipsometry and requires thick layers.

our study presents the possibility of evaluating the inhomogeneity in depth of the refractive index of thinner transparent films from monochromatic ellipsometry at various angles of incidence. We propose a method which is based upon the determination of the best experimental conditions (set of angles of incidence and wavelength) leading to the minimal uncertainty one can expect on the physical parameters to be determined.

We consider the case of a Al₂O₃ layer deposited on an InP substrat, and we characterise its optical profile by monochromatic ellipsometry.

- D-IX/P16** MAGNETOLUMINESCENCE MEASUREMENTS OF TWO-DIMENSIONAL HOLE GAS IN MAGNETIC FIELD, M. Ciorga, L. Bryja, J. Misiewicz, Wrocław University of Technology, Institute of Physics, Wyspińskiego 27, 50-370 Wrocław, Poland; O.P. Hansen, University of Copenhagen, Denmark

We performed magnetophotoluminescence measurements of Al_{0.5}Ga_{0.5}As/GaAs structures in magnetic field up to 6 T both in Faraday and Voigt configurations.

Energy shift of H-band shows exciton-like, non-linear dependence on magnetic field but its value is greater than that for GaAs excitons one. In Faraday configuration we can see very small spin splitting between lines observed in s₊ and s₋ polarisation. None splitting was observed in Voigt configuration between lines measured in s and p polarisation.

From temperature dependences energy of H-band emission was derived.

- D-IX/P17** OPTICAL STUDY OF THE INDIUM ACCUMULATION IN STRAINED QUANTUM WELLS, F. Hassen, H. Sghaier, H. Maaref and R. Murray*, Laboratoire de Physique des Semiconducteurs, Département de Physique, Faculté des Sciences, 5000 Monastir, Tunisia; *IRC Semiconductor Imperial College, London SW2BZ, UK

Indium surface segregation is known to occur during the growth of InGaAs alloys by Molecular Beam Epitaxy (MBE). This phenomenon can be characterised in-situ techniques and ex-situ techniques i.e. photoluminescence (PL) experiments.

Many models have been published about the study of In surface segregation depending on the growth temperature and other parameters, for example J. Nagle et al. have demonstrated that the segregation is not only sensitive to the substrates temperature, but also much more to the V/III ratio. In samples where In surface segregation occurs, it was shown by H. Toyashima et al. that the amount of In atoms which is not incorporated into the alloys, corresponding to the Monolayers (ML) thickness of InAs after the growth of the nth layer of In_xGa_{1-x}As and a model was proposed for this subject.

In this paper we will show the effect of the Indium accumulation in the last layer of the nominal quantum well (QW) on the position of the electron and hole energy levels in QW and try to have our experimental results (PL, PLE) fit with a simple model of the band offset.

To identify the PLE transitions, we have modified the model of Indium surface segregation proposed by Nagle et al. by introducing an adjustable parameter x, which is associated to the quantity of Indium atoms accumulated x changes from well to well even in the same sample. For large nominal well width and/or Indium concentration, this induces the existence of a second photoluminescence line (shoulder) in the low energy side of the main one. It can be associated to the transition 2D-3D growth mode and the appearance of self-organised quantum dots QDs.

- D-IX/P18** COMPUTER SIMULATION OF AlGaAs/GaAs SUPERLATTICES GROWTH BY LPE, R.Kh. Akchurin, A.A. Voshkin, Moscow State Academy of Fine Chemical Technology, Vernadskogo pr., 86, 117571 Moscow, Russia. The calculation model has been developed to simulate low temperature short-time "capillary" epitaxial growth of AlGaAs/GaAs superlattices by liquid phase epitaxy. It has shown according to results of simulation that the thin layer (< 10 nm) heterostructures with sharp interfaces can be successfully grown by this technique. Influence of the growth conditions such as the growth temperature, capillary channel thickness, substrate-melt contact time, initial supercooling and flowing regime of liquid upon composition and thickness uniformity of epitaxial layers is discussed. Computer simulation has allowed to establish of optimal combination of LPE growth parameters for AlGaAs/GaAs superlattices forming.
- D-IX/P19** RAMAN CHARACTERIZATION OF STRAIN RELAXATION EFFECTS IN HIGHLY-DOPED p-TYPE GaAs/GaAsP EPITAXIAL LAYERS, A.V. Subashiev, State Technical University, 195251 St. Petersburg, Russia, Yu. Davydov, I. N. Goncharuk, A. N. Smirnov, O. V. Kovalenkov, and D. A. Vinokurov, Ioffe Physicotechnical Institute, 194021 St Petersburg, Russia. Raman spectroscopy has been applied to study the misfit strain in MOCVD-grown heavily p-doped GaAs-on-GaAsP layers with varying thickness and substrate composition. Abrupt narrowing of the LO-phonon Raman line is observed for the large values of misfit accompanied by the anomalous shift of the Raman line to the low-frequency side. The theoretical analysis showed that the effect is due to the interband heavy hole - light hole transitions in the p-doped layer. The narrowing is due to the switching off the interband transitions when the valence band splitting exceeds LO - phonon frequency. Accommodation of the lattice misfit in the heteroepitaxial growth of GaAs layers substrates has been studied. We have found that the strain relaxation for $x=0.1-0.3$ reduces misfit to 80 % but stays constant up to 0.3 μm layer thickness.
- D-IX/P20** Al/Al₂O₃ MULTILAYERS DEPOSITION / RELATIONSHIP TO ELECTRICAL AND MECHANICAL PROPERTIES, C. Le Paven, S. Labdi, Ph. Houdy, L.M.N. Université d'Evry Val d'Essonne, Boulevard des Coquibus, 91025 Evry Cedex, France. In this paper, we have studied the effect of the nanometric scale on the mechanical and electrical properties of Al/Al₂O₃ multilayers. Films have been deposited by reactive RF sputtering. Single layer aluminium films exhibit high growth rates, resulting in damaging high rugosity : sputtering deposition was performed at low argon pressure and RF power, and optimisation was done by varying substrate temperature from - 196°C to 450°C. Alumina deposition was optimised versus oxygen films stoichiometry and characterised in situ by X-ray photoelectron spectroscopy (XPS) : 20% oxygen partial pressure was necessary to obtain stoichiometric Al₂O₃ films. Two types of 10 periods Al/Al₂O₃ multilayers were elaborated : first, keeping the value of the period constant (20 nm), different alumina thickness were investigated ; second, choosing 1:1 Al : Al₂O₃ ratio, period thickness was gradually lowered from 40 nm to 2 nm. Surface and cross section morphology, including thickness determination, were investigated by scanning electronic microscope (SEM). Structural characterisation was performed by X-ray diffraction and X-ray grazing incidence reflectivity. To study tribological behaviour, pin-disk experiments were carried out, giving the friction coefficient value. Films resistance from 4K to 300K was measured by classical four probe technique in helium cryostat.
- D-IX/P21** OBSERVATION OF CONFINED AND INTERFACE PHONONS IN GaAs/AlAs SUPERLATTICES GROWN BY MBE ON FACETED (311)A,B AND (100) SURFACES, V.A. Volodin, M.D. Efremov, V.V. Preobrazhenski, B.R. Semyagin, Institute of Semiconductor Physics SB RAS, pr. Lavrentjeva 13, Novosibirsk 630090, Russia ; V.V. Bolotov, V.A. Sachkov, Institute of Sensor Microelectronics SB RAS, pr. Mira 55a, Omsk 1 644077, Russia. Phonon spectra of GaAs/AlAs superlattices (SLs) grown on facet surfaces (311)A,B and (100) surface were studied using Raman spectroscopy in far-from-resonance and in near-resonance conditions. Thickness of GaAs layers in the studied SLs was varied from 0.17 nm to 1.7 nm, thickness of AlAs barriers was 1.36 nm. In Raman spectra of SLs grown on faceted surfaces (311)A and B the peaks corresponding to scattering on GaAs-like and AlAs-like interface phonons were detected even in far-from-resonance conditions. But in the case of SLs grown on (100) surface the interface phonons were not active in Raman scattering both in far-from-resonance and in near-resonance conditions. So, one can assume that activity of the interface phonons in Raman scattering is induced by regular corrugation of (311)A and B GaAs/AlAs interfaces. The transformation of interface phonon frequencies depending on scattering geometries was studied. The difference of interface mode frequencies for SLs grown on (311)A and (311)B surfaces was observed, what can be result of different structure of these interfaces. The numerical calculations of frequencies of confined and interface phonon modes were carried out, the good correlation with experiment was observed. This work was supported by Russian Fund of Basic Research Grant No 97-02-18422.
- D-IX/P22** RAMAN STUDY OF OPTICAL PHONONS CONFINED IN QUANTUM OBJECTS FORMED BY MBE OF GaAs/AlAs SUPERLATTICES CONTAINING GaAs SUBMONOLAYERS ON (311)A,B AND (100) SURFACES, V.A. Volodin, M.D. Efremov, V.V. Preobrazhenski, B.R. Semyagin, Institute of Semiconductor Physics SB RAS, pr. Lavrentjeva 13, Novosibirsk 630090, Russia ; V.V. Bolotov, V.A. Sachkov, Institute of Sensor Microelectronics SB RAS, pr. Mira 55a, Omsk 1 644077, Russia. Strong confinement of GaAs-like optical phonons within approximately one monolayer of surrounding AlAs and strong dependance of confined phonon frequencies on size and structure of GaAs insertions were believed to give an appropriate tool for testing of structure of quantum objects (wetting layers, quantum wires or dots) formed in first stages of heteroepitaxial growth. GaAs on different surfaces. Raman technique was applied to study phonon spectra of superlattices (SLs) containing submonolayers (0,17 nm) of GaAs divided by 1.36 nm AlAs layers grown on facet surfaces (311)A,B and (100) surface. The thickness of layers was determined by growth time calibrated by RHEED oscillations for the case of control growth of the same thickness on (100) surface of GaAs. It was observed that Raman spectra of these structures were not like spectra of local vibration of Ga in AlAs matrix. In the case of (100) surface the triplet structure of Raman peak corresponding to scattering on GaAs-like confined longitudinal phonons was observed. The calculation of phonon spectra using the model of rigid ions gives only singlet peak. It seems likely that triplet structure appears due to additional lateral confinement of GaAs-like optic phonons in formed quantum objects. Using selection rules for (311)A and B surfaces, different polarization geometry of Raman scattering was applied to study longitudinal and two modes of transverse optical phonons. The dublet structure of Raman spectra was observed. Positions of peaks depend on polarization geometry detecting two various TO modes. That can be indirect evidence of anisotropic structure of formed GaAs quantum objects. This work was supported by Russian Fund of Basic Research Grant No 97-02-18422.
- D-IX/P23** OPTICAL STUDIES OF CARRIER TRANSPORT PHENOMENA IN CdSe/ZnSe FRACTIONAL MONOLAYER SUPERLATTICES, T.V. Shubina, A.A. Toropov, S.V. Ivanov, S.V. Sorokin, P.S. Kop'ev, Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia and G. Posina, J.P. Bergman, B. Monemar, University of Linköping, 581 83 Linköping, Sweden. Recent studies of CdSe/ZnSe strained nanostructures have revealed unique interface properties like formation of 2D CdSe islands with atomically sharp interfaces in thin layers (with the nominal thickness less than 1 monolayer (ML)) as well as growth of relatively large 3D clusters in the CdSe layers close to the critical thickness ($\sim 3\text{ML}$). In this paper we focus on optical studies of short-period CdSe/ZnSe fractional-monolayer superlattices (SLs), aimed at elucidation of vertical carrier transport along the growth axis. For this purpose a set of specially designed structures was grown, which contain the SL with an embedded enlarged ZnCdSe quantum well (QW). The samples differ in the nominal thickness of the constituent CdSe layers and in the SL period. To characterize the SL transport properties, we studied the low-temperature photoluminescence (both cw and time-resolved) emitted by the enlarged QW located far away from the region of the carriers generation. Extremely efficient vertical transport is observed for the CdSe insertion thickness being in the range 0.1-1.5 ML, which confirms formation of the SL of the ordered extended 2D CdSe islands.

- D-IX/P24** ELECTRIC-FIELD-INDUCED RAMAN SCATTERING AT ZnSe/GaAs INTERFACES, O. Pagès, A. Zaoui, M. Certier, J.P. Laurenti, D. Bormann*, B. Khelifa*, O. Briot** and R.L. Aulombard**, Laboratoire de Spectrométrie Optique de la Matière, Université de Metz, 1 Bd Arago, 57078 Metz, France, *Equipe de Spectrométrie Raman, Université d'Artois, Rue Jean Souvraz, 62307 Lens, France, **Groupe d'Etude des Semiconducteurs, associé au CNRS (URA 357), Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34095 Montpellier, France

Electric-field-induced Raman scattering (EFIRS) of longitudinal optical (LO) phonons in the low and high field limits are currently discussed in semiconductors within the frameworks of (i) the phenomenological perturbative theory of morphic effects and (ii) the microscopic treatment which considers the "atomic displacement" and "Franz-Keldysh" scattering mechanisms. Both approaches were used for static electric fields either homogeneous externally applied or inhomogeneous associated with electronic band bending in space charge regions (SCR) [1, 2]. However a limit should be reached in the second case as none of these two approaches does explicitly incorporate the inhomogeneous character of the electric field. The aim of this work is to investigate to what extent this character may explain the non-simultaneous activation of EFIRS on both sides of ZnSe/GaAs heterointerfaces although continuity in the displacement vector is expected.

N-ZnSe (type 1) and p-ZnSe (type 2) naturally doped 1 μ m thick layers were grown by MOCVD on the same (100) semi-insulating GaAs substrate. Conventional Raman spectra recorded in backscattering condition from types 1 and 2 heterostructures exhibit LO phonon-plasmon coupled modes. These arise from the space charge region on the substrate side. In type 1 samples a straightforward comparison of the integrated intensities of the interfacial LO phonon-plasmon coupled mode, labelled Y, and the LO_{ref} mode from a reference substrate shows that the Y mode undergoes EFIRS effect. This is due to the inhomogeneous electric field associated with the electronic band bending in the space charge region. Line-shape analysis of the LO phonon-plasmon mode from type 2 samples, labelled X, could only be achieved when incorporating plasma inhomogeneity. Average electric fields as high as 10^{16} V/cm, typically involved in EFIRS effects on pure LO modes, were indirectly deduced from the inferred carrier-density profile. However no EFIRS effect has to be considered since no evolution is observed in the strength of the X mode under increasing illumination.

The aim of the paper is to investigate why the strength of the X mode from the SCR is not sensitive to EFIRS. With this end in view the interfacial region on the substrate side of air-clived type 2 (110) surfaces was analyzed by using the microprobe technique. EFIRS effects are directly observed on the GaAs side. It is deduced that the inhomogeneous character of the electric field in the space charge region brings additional conditions to the activation of EFIRS. Besides, basic electronic and vibrational informations upon the nature of the II-VI/III-V interfaces are deduced in relation with the growth conditions.

[1] D.J. Olego, Phys. Rev. B39, 12743 (1989).

[2] J. Wagner, A.L. Alvarez, J. Schmitz, J.D. Ralston, and P. Koidl, Appl. Phys. Lett. 63, 349 (1993).

- D-IX/P25** TRANSMISSION ELECTRON MICROSCOPY STUDY ON Cu-Ni-SiO₂ THIN FILM ELECTRICAL RESISTORS, J.J.T.M. Donkers, Philips Centre for Manufacturing Technology, J.J. van den Broek and R.A.F. van der Rijt, Philips Research, Eindhoven, The Netherlands

A transmission electron microscopy study has been performed on a new promising resistive material for very high ohmic resistors: Cu-Ni-SiO₂. The main objective of the study was to find a thin film with an absolute value of the temperature coefficient of the resistivity, $|TCR| < 25$ ppm/K and a square resistance, $R_s \approx 1$ k Ω . A low TCR component, Cu₆₀Ni₄₀, was diluted by the non-conducting component SiO₂ to achieve a high resistivity. Upon heat treatment significant changes of the electrical properties of the films were observed. To correlate these changes to the film's microstructure, many samples have been prepared for TEM analysis. Films have been studied that were deposited on the standard substrate, sintered Al₂O₃, as well as on so-called TEM windows, both as-deposited and (in-situ) annealed.

Drastical changes of electrical properties upon heat treatment are explained in terms of the microstructure. After deposition CuNi grains, with sizes of 5 to 10 nm, are surrounded by amorphous SiO₂, explaining the high resistivities and strongly negative TCR. Upon annealing of the films the resistance and absolute value of the TCR decrease, caused by the formation of a conducting CuNi network. At higher temperatures the resistance is seen to increase, while the TCR again becomes more negative. These changes are caused by the formation of large copper-rich crystals with grain sizes up to 100 nm. The increase of the absolute value of the TCR is caused by the shift of the composition in the conducting network. Formation of the copper-rich crystals can be avoided by covering the resistor film with an additional thin SiO₂ layer.

- D-IX/P26** TEM AND AFM STUDY OF PEROVSKITE CONDUCTIVE LaNiO₃ THIN FILMS PREPARED BY METALORGANIC DECOMPOSITION, Aidong Li*, Di Wu*, Zhiguo Liu*,**, ChuanZhen Ge*, Peng Lu* and Naiben Ming*, **, *National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R. China; **, Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, China

Perovskite conductive LaNiO₃ (LNO) films were prepared by metalorganic decomposition. The films were obtained by spin-on pyrolysis in air on various substrates and then annealing at various temperature. The effect of different thermal treatments, annealing temperature and substrates on crystallinity, orientation, surface morphology and conductive behavior of LNO films was studied. The results obtained by TEM and selected area electron diffraction indicated that in the thermal treatment process the oxygen diffusion into the film is the critical step in the fabrication of good metallic LNO films at lower grown temperature. Various surface morphology including grain size, orientation and roughness was recorded by AFM. Epitaxial LNO films could be fabricated on SrTiO₃.

- D-IX/P27** ADHESIVE AND VIBRATORY PHENOMENA AT SHOCK OF METALLIC NANOPARTICLES STUDIED BY MOLECULAR DYNAMICS SIMULATION, V.V. Pokropivny, V.V. Skorokhod, Institute for Problems of Materials Science, 252142 Kiev, Ukraine and A.V. Pokropivny, Yu.G. Krasnikov, Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia

The processes of iron nanoparticles shock are computer simulated at the atomic level by molecular dynamics technique. The correlation between the structure transformation and variations of energy and force of adhesion, adhesive bond number, viscosity of contact is analysed. The adhesive-vibratory effect is observed. Acoustic and optical phonon spectra for vibrations of mass centres and single atoms are calculated. The problems of interatomic potentials design and development of this technique for nitride and boride (TiN-TiB) nanoparticles are discussed. Velocity dependent change of atomic mechanisms of shock interactions is discussed. During a shock with small velocity the joint action both the adhesive forces and impact pressure leads to joint dynamically steady vibratory and translation movement. At higher velocity, when the atomic processes of relaxation and shock occur simultaneously, vibrations are shown to transform into inelastic flow, amorphization and fracture of nanoparticles. At a near-sound velocity the particles are shown to smash into splinters. The concept of new devices is proposed based on the resonance principle of powders compacting and coating activation by means of ultrasound treatment synchronized with shock influence.

D-IX/P28 STUDY OF SURFACE SPIN ORDER IN EPITAXIAL PEROVSKITE MANGANITE THIN FILMS, M.B. Hunt, A. Llobet and L. Ranno, Laboratoire Louis Néel, Polygone CNRS, BP 166, 25 avenue des Martyrs, 38042 Grenoble Cedex 09, France and R. Borges, Physics Department, Trinity College, Dublin, Ireland

There is considerable interest in the use of thin films of half metallic ferromagnetic perovskite oxides of manganese as sources of spin polarised electric current. An important possible application is their use as electrodes in magnetically driven spin valve tunnel junctions operating with high field sensitivity at ambient temperatures. It has been observed in actual junctions however, that although tunnelling magnetoresistances of several hundred % can be achieved at 4K, this falls to zero well below the Curie temperature of the electrodes. It is at present unclear whether this is an intrinsic effect or an extrinsic one related, for example, to the existence of alternate non-tunneling conduction paths between the two electrodes. It is of the greatest importance for the further development of these devices that the source of this effect be identified. A likely candidate is the presence of surface spin disorder, which could depolarise any ejected current.

We present a study of magnetisation as a function of thickness in epitaxial films of $\text{La}_x\text{Ca}_{3-x}\text{MnO}_3$, produced by pulsed laser deposition, the goal of which is to determine whether there is magnet disorder at the surface. The data are consistent with the existence of a surprisingly thick 5nm surface layer with zero magnetic moment. This is in conflict with magnetic dichroism and spin polarised photoemission studies on similar materials. A spin polarised neutron reflectivity investigation is to be undertaken in order to clarify this issue.

E-MRS'98 SPRING MEETING



SYMPOSIUM E

Thin Film Materials for Large Area Electronics

Symposium Organizers

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SYMPOSIUM E

Tuesday, June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - Microcrystalline and Amorphous Silicon: Plasma Deposition

Chairperson: B Equer, LPICM, Ecole Polytechnique, Palaiseau, France

- E-I.1** 9:00-9:40 - Invited - **GROWTH MECHANISM OF MICROCRYSTALLINE SILICON OBTAINED FROM REACTIVE PLASMAS. A. Matsuda**, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305-8568 Japan
Hydrogenated microcrystalline silicon thin films are prepared from a variety of methods, e.g., glow-discharge decomposition of silane-hydrogen mixture, chemical transport of cooled silicon materials to heated substrate, hydrogen plasma treatment of thin amorphous silicon layers, etc... In each process, different mechanisms have been proposed, i.e., sufficient surface diffusion of film precursors on the film-growing surface, chemical equilibrium reactions between etching and growth, and hydrogen chemical annealing reactions in the sub-surface region (growth zone), respectively. In this talk, our recent experimental results are shown for the discussion of the microscopic growth process of microcrystalline silicon. Substrate temperature dependence of silicon films under extra pure plasma CVD conditions shows that microcrystalline silicon is grown even at room temperature, larger crystallite size more than 100nm is obtained at 350°C, and it turns to amorphous above 450°C. Layer-by-layer growth with mechanical shutter gives no clear evidence of the presence of chemical annealing process. These results guide us to the detailed discussion for the microscopic mechanism underlying the low temperature growth process of microcrystalline silicon films from reactive plasmas.
- E-I.2** 9:40-10:00 **DEVICE QUALITY MICROCRYSTALLINE SILICON DEPOSITED FROM SiF_4/H_2 MIXTURES AT LOW TEMPERATURE, R. Brenot**, B. Drévillon, P. Roca i Cabarrocas and R. Vanderhaghen, Laboratoire de Physique des Interfaces et des Couches Minces, UMR 7647 du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France
Direct deposition of high mobility low temperature microcrystalline silicon ($\mu\text{-Si}$) is a challenging issue for Thin Film Transistors (TFT's). Thanks to its high etching efficiency, SiF_4 is a very good candidate to achieve this objective. Therefore, $\mu\text{-Si:H}$, F was deposited in a conventional RF (13.56 Mhz) Plasma Enhanced Chemical Vapor Deposition reactor from SiF_4/H_2 mixtures at temperatures below 300°C, in various conditions such as H_2 dilution. The growth kinetic was studied by in-situ Spectroscopic Ellipsometry. Real-time fitting of these kinetic spectro-ellipsometric trajectories have revealed the evolution of crystalline fraction at both interfaces as well as the surface roughness during deposition. The structure of the films has also been analyzed by Raman Spectroscopy and by X-Ray diffraction. Transport properties of the films were investigated by conductivity measurements and by Time Resolved Microwave Conductivity. This latter method gives access to the microwave mobility of electrons and to the effective lifetime of excess carriers. Contrary to $\mu\text{-Si:H}$ deposited from SiH_4/H_2 mixtures, full crystallization of the top interface, very low surface roughness (less than 5 nm) and microwave mobility above $20 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ have been obtained. $\mu\text{-Si:H}$, F appears therefore as a very promising material for TFT's.
- E-I.3** 10:00-10:20 **PROPERTIES OF POLYCRYSTALLINE SILICON FILMS PREPARED FROM FLUORINATED PRECURSORS, Swati Ray**, Sukti Hazra, Energy Research Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
Polycrystalline silicon films have been prepared from fluorinated precursors by PECVD technique. In this work, electronic and structural properties of polycrystalline silicon films with phosphorous doping have been investigated. Usually good quality doped poly-Si films have been prepared using higher processing temperature $\geq 600^\circ\text{C}$ or by layer by layer technique. Here using simple PECVD technique and fluorinated gas device quality silicon films have been developed at 250°C . For undoped poly-Si films dark conductivity and its activation energy obtained were $1.6 \times 10^{-6} \text{ Scm}^{-1}$ and 0.37 eV respectively under optimised deposition condition. Grain size observed from SEM varies from 2 to $6 \mu\text{m}$ whereas the crystallite size calculated from X-ray diffraction studies was 327 \AA . The main crystalline peak is $\langle 111 \rangle$, part of the optimised film was $1.45 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1}$. Due to use of SiF_4 as source gas instead of SiH_4 precursors like $\text{SiF}_n\text{H}_{4-n}$ ($n+m \leq 3$) and HF have been produced which are much more active so far structural relaxation is concerned. In order to dope the films both $\text{PH}_3+\text{SiF}_4+\text{SiH}_4$ and PH_3+SiF_4 mixture have been used whereas the later is more effective at low hydrogen dilution. N-type poly-Si films with dark conductivity $8 \times 10^{-3} \text{ Scm}^{-1}$ has been obtained. This value is higher than that achieved through layer by layer technique using the same gas mixture. The absorption properties of the film changed significantly ($E_{0.4} = 1.83 \text{ eV}$) with doping. The structural properties of the materials are being studied now.
- E-I.4** 10:20-10:40 **CONTROL OF HIGH DENSITY PLASMA WITH NO MAGNETIC FIELD FOR LARGE-SCALED ELECTRONICS, H. Shirai** and T. Arai, Saitama University, 255, Shimo-Okubo, Urawa-shi, Saitama, 338, Japan
High density plasma, such as Electron Cyclotron Resonance (ECR), Inductive Coupling Plasma (ICP), and Surface Wave Plasma (SWP) have been used as deposition and etching processes. However, for more than 12-inch diameter substrates, it is very difficult to simply scale up the chamber for conventional plasma sources because of magnetic coil. We will present a low temperature, uniform, high density μ -wave plasma (2.45 GHz) with a spokewise antenna for large-area hydrogenated amorphous and microcrystalline silicon (a-Si:H and $\mu\text{-Si:H}$) films deposition processes from dichlorosilane (SiH_2Cl_2) and H_2 . The plasma is uniform within $\pm 5\%$ over a diameter 22 cm in several mTorr region. The plasma density, $> 10^{11} \text{ cm}^{-3}$ and low electron temperature of 2 eV in Ar plasma with no magnetic fields. The influence of discharge pressure, power and homogeneities have been characterized using a Langmuir probe together with the film optical electrical properties.

10:40-11:20

BREAK

E-I.5 11:20-11:40

CONTROL OF ORIENTATION FROM RANDOM TO (220) OR (400) ORIENTATION IN POLYCRYSTALLINE SILICON FILMS, T. Kamiya, K. Nakahata, A. Miida, C.M. Fortmann and I. Shimizu, The Graduate School, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

The orientation of crystallites in polycrystalline silicon (poly-Si) thin films are governed by surface reaction kinetics. These reaction kinetics were systematically varied during microwave plasma chemical vapor deposition through the deposition parameters including: substrate temperature ($\sim 360^\circ\text{C}$), source gas flow rates and source gas composition. SiF_4 , H_2 and Ar gas mixtures were among the varied parameters. Reaction pressure and microwave power were fixed to 400mTorr and 200W respectively. Film thickness' were varied from 0.5 to 4 μm .

XRD profiles of the films were used to establish orientation. We found that (220) preferential growth was obtained with $\text{Ar}/\text{H}_2/\text{SiF}_4$ gas flow rates of 60/15/30sccm (respectively). Under 60/10/90sccm flow rates the orientation of the 0.5 μm thick films was almost random. This random orientation slowly changed to (400) with increasing films thickness, thick films (2 μm) showed strong (400) orientation. The TO Raman scattering peak at $\sim 510\text{cm}^{-1}$ had a very small width (7.6cm^{-1}); while, the pseudo-dielectric function measured by spectroscopic ellipsometer showed sharp crystalline peaks at ~ 3.2 and $\sim 4.2\text{eV}$, indicating that these (400) films have a very low structure fluctuation or strain as these parameters are similar to single crystal silicon. Details and other results will be presented at the conference.

E-I.6 11:40-12:00

MICROCRYSTALLINE SILICON GROWTH ON a-Si:H: EFFECTS OF HYDROGEN, P. Roca i Cabarrocas and S. Hamma, Laboratoire PICM (UPR 258 CNRS), Ecole Polytechnique, 91128 Palaiseau, France

It is well known that atomic hydrogen plays a crucial role in the formation of microcrystalline silicon films. The growth of this material is characterized by four phases (incubation, nucleation, growth and steady-state) and the kinetics of this growth is governed by the flux of atomic hydrogen towards the substrate, which can be easily modified in the layer-by-layer technique [1]. Moreover, due to the long range diffusion of hydrogen there is a modification of the a-Si:H substrate [2].

In this paper we study this modification by means of in-situ ellipsometry and SIMS analysis. The substitution of hydrogen by deuterium in the layer-by-layer formation of $\mu\text{c-Si}$ films on different a-Si:H substrates allows to compare the long range effects deduced from the analysis of the spectroscopic ellipsometry measurements with the deuterium profiles deduced from SIMS analysis. The importance of the long range effects of hydrogen is discussed in the particular case of p-i-n solar cells where the electric field, which develops between the p and n layers, can have a strong effect on hydrogen diffusion.

[1]. S. Hamma and P. Roca i Cabarrocas, J. Appl. Phys. 81 (1997) 7282.

[2]. S. Hamma and P. Roca i Cabarrocas, Thin Solid Films 296 (1997) 94.

E-I.7 12:00-12:20

STRUCTURE OF POLYCRYSTALLINE Si FILMS DEPOSITED AT LOW TEMPERATURE BY PLASMA CVD ON SUBSTRATES EXPOSED TO DIFFERENT PLASMA, S. Moniruzzaman, R. Tsuchida, Y. Kurata, T. Inokuma and S. Hasegawa, Faculty of Engineering, Kanazawa University, Kanazawa 920, Japan

The $\langle 110 \rangle$ textured polycrystalline silicon (poly-Si) films were deposited by rf plasma CVD from $\text{SiH}_4/\text{SiF}_4$ at 300°C . In the application of poly-Si to thin-film transistors (TFTs), crystallinity and crystal structure of films, such as orientation of grains, grain size and the nature of grain boundary, profoundly affect the TFT characteristics. The structural change of poly-Si films due to plasma treatments of glass substrates (corning 7059), caused by exposing them to CF_4 , N_2 and/or H_2 plasma with different pressure before the film deposition, were investigated by XRD, Raman scattering and AFM measurements. Without the plasma treatments, the resultant films were found to be amorphous. However both XRD intensity and grain size increased at first, and then decreased with increasing the pressure in the above-mentioned plasma treatments for the substrates. The maximum grain sizes were found to be around 150nm. These result were corresponded well with the results of Raman scattering and AFM measurements. The result indicates that the plasma treatments on substrates improve the crystalline quality of poly-Si at low temperature.

12:20-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION I - Microcrystalline and Amorphous Silicon: Plasma Deposition (continued)**Chairperson: B. Equer, LPICM, Ecole Polytechnique, Palaiseau, France****E-I.8** 14:00-14:20

DEPOSITION DEFECT AND WEAK BOND FORMATION PROCESSES IN a-Si:H, J. Robertson, Engineering Dept., Cambridge University, Cambridge CB2 1PZ, UK; M.J. Powell, Philips Research Labs, Redhill, Surrey RH1 5HA, UK

A growth model is developed to describe the temperature variation of the weak bond density, dangling bond density and hydrogen content of PECVD a-Si:H. It is accepted that a-Si:H grows by a process in which SiH₃ radicals physisorb on the mainly H-saturated surface, move about, to react with surface Si dangling bonds formed by H abstraction by SiH₃ radicals [1]. Ganguly and Matsuda [2] proposed that bulk dangling bonds arise by being buried during growth by interplay between these processes. We argue that the surface dangling bond density needed for reasonable growth rates is too high for the final bulk defect density. A growth model must also account for the weak temperature dependence of H content, equivalent to an activation energy of ~0.02eV. H elimination is often assumed to occur by recombination of two surface dangling bonds, but this would give too high an activation energy. A new growth model is developed, emphasising the importance of hydrogen elimination. This is argued to occur in the subsurface growth zone by H rearrangement at H₂*-like centres, leaving weak Si-Si bonds which form the valence band tail. In this way, rather than defects being formed at growth, growth produces weak bonds and dangling bonds then form by equilibration and conversion from weak bonds.

[1] R. Robertson, A. Gallagher, J. Chem Phys 85 3623 (1986)

[2] G. Ganguly, A. Matsuda, Phys Rev B 47 3661 (1993)

E-I.9 14:20-14:40

DEPOSITION OF MICROCRYSTALLINE SILICON AND SILICON ALLOYS IN AN INTEGRATED DISTRIBUTED ELECTRON CYCLOTRON RESONANCE PECVD REACTOR, P. Bulkin, A. Hofrichter, R. Brenot and B. Drévilion, Laboratoire de Physique des Interfaces et des Couches Minces, UMR 7647 du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France

We present results regarding the deposition of μ c-Si and silicon alloys in an integrated distributed electron cyclotron resonance (IDECR) reactor. ECR plasma creates high electron density at low pressure and induces high dissociation rates of precursors. That makes the deposition of μ c-Si from pure silane plasmas possible. It also allows for pre-cleaning of the substrates and subsequent deposition of dielectric layers on top of μ c-Si films, making IDECR well adapted for electronic applications.

Since it is known, that structure of μ c-Si is changing during the growth we followed deposition by kinetic phase modulated ellipsometry (PME). Such approach allowed us to study growth of μ c-Si and determine the evolution of crystalline volume fraction. Combining spectroscopic PME and real time kinetic allows to optimise processes on both interfaces. Silica and Si₃N₄ were also grown and influence of process conditions onto the kinetics and film properties was investigated. High quality of the films and fast growth rates confirm that reactors, based on IDECR principle, are emerging as strong competitors among high-density plasma deposition systems.

E-I.10 14:40-15:00

HYDROGENATED AMORPHOUS AND NANOCRYSTALLINE P TYPE SILICON FILMS, DEPOSITED BY HOT WIRE AND PECVD TECHNIQUES, H. Aguas, I. Ferreira V. Silva, E. Fortunato, R. Martins, DCM/FCT-UNL, Quinta da Torre, 2825 Monte de Caparica, Portugal

In this work we studied the role of the deposition conditions on the compositional, electrical and optical properties of hydrogenated amorphous and nanocrystalline p type silicon thin films produced in a Hot Wire system using a gas mixture of 44.2% of SiH₄, 33.4% of CH₄, 22.2% of H₂ and 2000 ppm of B₂H₆. This gas mixture was also dissolved in a H₂ gas, at different percentages. For comparing the results we also produced similar films using a diode type PECVD system. The Hot Wire films were produced at a substrate temperature of 300°C, a pressure varying from 0.2 to 0.7 Torr, and tension applied to the tungsten filament varying from 220 to 340V, 50Hz. The percentage of hydrogen dilution used during deposition varied from 22.2 % to 99.6%. The Hot Wire films show good growth rate ranging from 10 to 20 Å/s compared to the PECVD films that show a smaller growth rate ranging from 1 to 5 Å/s. The Hot Wire films presented an optical gap similar to the PECVD films ranging from 1.6 to 2.1 eV while we notice a great influence of the deposition parameters on the dark conductivity, that can vary from 8.87x10⁻⁵ to 25.07 (Ωcm)⁻¹, with activation energies varying from 0.627 eV to 0.076 eV, respectively. These results, together with the ones due to infra-red measurements will be analysed for both type of films produced, aiming to select the conditions that lead to the production of high quality electronic materials for device applications.

SESSION II - Microcrystalline and Amorphous Silicon: Laser Crystallisation**Chairperson: B. Drévilion, LPICM, Ecole Polytechnique, Palaiseau, France****E-II.1** 15:00-15:40 - Invited -

ADVANCED EXCIMER LASER PROCESSES FOR SILICON THIN-FILM TRANSISTOR, M. Matsumura, Department of Physical Electronics, Tokyo Institute of Technology, O-okayama, Meguro-Ku, Tokyo 152-8550, Japan

Excimer-laser processes will be reviewed aiming at an application to ultra-high performance TFTs on non-heat-tolerant glass substrate. And it is pointed out to be essential to enlarge the grain size dramatically. This is because the grain boundary related problems, such as the low field effect mobility, high leakage current and also their large fluctuation among TFTs, are solved simultaneously and the "system-on-panel" technology becomes a practical target of development. The key concept of the ultra-large grain growth is to control the motion of the melt/solid interface at will. This can be achieved by modulating laser-light intensity on the sample surface. A phase-shift technique, the common technique in the lithography field, is the answer to this requirement. Two-dimensional arrays of grains with as large as 8mm were grown by single shot irradiation of laser light pulse by using this method. This method will play a important role not only to TFTs but also solar cells and ULSIs (SOIs).

SYMPOSIUM E

E-II.2 15:40-16:00

LARGE-GRAINED POLYCRYSTALLINE SILICON ON GLASS BY COPPER VAPOR LASER ANNEALING, J.R. Köhler, R. Dassow, R. B. Bergmann and J.H. Werner, Universität Stuttgart, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, Germany

Recent improvements in excimer laser crystallization of amorphous silicon on oxidized wafers result in grain sizes of several tens of μm utilizing the sequential lateral solidification process. The use of excimer lasers limits the pulse frequency to 400 Hz, and therefore restricts the scanning speed to 0.3 mm/s. The high pulse energy of more than 100 mJ results in an inefficient transfer of the beam energy to the substrate, because more than 95 % of the energy is absorbed in a projection mask. In contrast to these conventional procedures, we use a copper vapor laser with 20 kHz pulse frequency and optics without projection mask, with the consequence of 10 mm/s scanning speed and high energy transfer efficiency. We apply this process to crystallize 0.4 μm thick amorphous silicon films on glass substrates. Transmission electron, scanning electron, atomic force microscopy and micro Raman spectroscopy serve to characterize the films. They contain large elongated grains 3 to 5 μm wide and several tens of μm in length with an intragrain defect density below $10^6/\text{cm}^2$. In addition we apply a modified process to produce films with a well-defined and controlled grain size between 1 and 10 μm . Thus, the size, location and number of grains per unit area can be tailored for various applications. A process analysis indicates the potential to crystallize 10 cm^2/s of amorphous silicon using copper vapor lasers. Our approach is therefore of interest for large area electronic devices such as thin film solar cells or thin film transistors.

16:00-16:30

BREAK

E-II.3 16:30-16:50

SINGLE SHOT EXCIMER LASER CRYSTALLIZATION AND LPCVD SILICON TFT's, Y. Ellen, K. Mourgues, F. Raoult, T. Mohammed-Brahim, O. Bonnaud, P. Boher*, D. Zahorski*, GMV, UPRESA au CNRS 6076, Université Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France; *SOPRA S.A., 26 rue P. Joigneaux, 92270 Bois Colombes, France

Excimer laser (ECL) crystallization of silicon films on low temperature substrates is one of the most promising technique for large-area polycrystalline silicon films. Crystallization technique using pulsed-ECL is characterized by films with high electrical properties but low uniformity. In this way, technology using single shot ECL with very large excimer laser (VEL) may be very promising. It is used here to crystallize undoped amorphous silicon films deposited by LPCVD which constitute the active layer of n-type thin film transistors. The LPCVD technique is the most commonly used deposition technique of silicon. It presents numerous advantages and the hydrogen content in the films, known to constitute a drawback in the crystallization process, is negligible (~ 1 at.%). Drain and source regions of the TFT's are in-situ doped using phosphine. The gate insulator is an atmospheric chemical vapor deposited SiO_2 layer. The process does not include any hydrogenation step. The performances of these TFT's are studied versus the laser fluences and the number of shots at fixed fluence.

An optimum fluence is highlighted from the behaviours of the subthreshold slope S and the threshold voltage V_T of these TFT's. The optimum occurs at lower fluence when the number of shots increases. The behaviour of the field effect mobility shows a maximum. The maximum occurs at lower fluence than that of the S and V_T optimum. Thus at low fluence, the effect of the shot number is more important on S and V_T parameters, which are more linked to the insulator-silicon interface, than on the mobility. The difference is explained from the energy actually absorbed at the film surface during the laser annealing.

E-II.4 16:50-17:10

SINGLE AREA EXCIMER LASER CRYSTALLIZATION OF AMORPHOUS SILICON FOR FLAT PANEL DISPLAY APPLICATIONS, P. Boher, D. Zahorski and M. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France

The obtention of polycrystalline silicon films on glass substrates with high electrical properties is now a key point for the new generation of flat panels displays. In particular the possibility to integrate fussy logic directly on the panel will extend the market of the next few years. In this respect, excimer laser annealing of amorphous silicon films appears has the more promising technique and is already used in production. Nevertheless one of the main drawbacks of this technique is the laser pulse recovery when using low power lasers. At SOPRA a high power excimer laser has been developed which can apply 45 Joules of total energy on the sample surface in one pulse. So 100 cm^2 of panel can be treated in one laser pulse and the recovery problem becomes less critical. Last results obtained with this new system in terms of laser performances, polycrystalline silicon structural quality and electrical results on TFT devices will be presented.

E-II.5 17:10-17:30

LATERAL GROWTH CONTROL IN EXCIMER LASER CRYSTALLISED POLYSILICON, L. Mariucci, R. Carluccio, A. Pecora, G. Fortunato, IESS-CNR, via Cineto Romano 42, 00156 Roma, Italy; P. Legagneux, D. Pribat, THOMSON-CSF, LCR, 91404 Orsay, France; D. Della Sala, ENEA Casaccia, Roma, Italy; J. Stoemenos, University of Thessaloniki, Greece

Recently, excimer laser crystallization (ELC) has become a key technology to fabricate polysilicon thin-film transistors (TFTs). When the Super Lateral Growth (SLG) mechanism is triggered, large ($>1 \mu\text{m}$) grains are formed and high performance (field-effect mobility $>300 \text{ cm}^2/\text{Vs}$) TFTs can be obtained. However, SLG process has a very narrow energy density window and is characterized by a strongly non-uniform grain size distribution. In this work we have investigated several approaches to achieve a control of the SLG-mechanism through lateral thermal gradients, established by the opportune modulation of the absorbed laser energy. To this purpose, three different patterned capping layers have been used. For the first structure we used SiO_2 stripes, 6 microns wide and 47 nm thick, acting as antireflective coating for the underlying amorphous silicon film. We observed that when the capped Si film is fully melted, the adjacent un-capped region, that cools first, acts as seed for the regrowth of the capped region. This results in elongated grains (maximum dimension 1-2 μm) at the stripe boundaries, forming a comb-like structure. In the second structure Si_3N_4 stripes, 6 micron wide and 149 nm thick, were used to cool faster the underlying silicon film (due to the high thermal conductivity of silicon nitride), while keeping unchanged the laser energy absorbed by the Si. In this case the lateral growth started from the capped regions towards the adjacent un-capped areas. Finally, we used, for the first time, patterned metal overlayers to reflect the laser radiation and create thermal gradients between the shadowed and illuminated regions. SEM and TEM analyses show that lateral growth can be easily triggered at the boundary between these two regions and elongated grains up to 2 μm have been observed.

E-II.6 17:30-17:50

SURFACE MELT DYNAMICS AND SUPER LATERAL GROWTH (SLG) REGIME IN LONG PULSE DURATION EXCIMER LASER CRYSTALLIZATION OF AMORPHOUS Si FILMS, E. Fogarassy, S. de Unamuno, CNRS, Laboratoire PHASE (UPR 292), BP 20, 67037 Strasbourg Cedex 2, France; P. Legagneux, F. Plais, D. Pribat, THOMSON LCR, Domaine de Corbeville, 91404 Orsay Cedex, France; B. Godard, M. Stehle, SOPRA SA, 26 rue Pierre Joigneaux, 92270 Bois Colombes, France

Excimer laser crystallization of amorphous silicon (a-Si) films appears very promising to prepare high quality polycrystalline-Si TFTs for the developing technology of large area electronics on cheap glass substrates. The use of high powerful pulsed lasers, working in the nanosecond duration regime, allows to deposit a large amount of energy in short times into the near surface region. Under suitable conditions, the irradiation leads to the rapid melting of the a-Si layer and its subsequent crystallization from the underlying amorphous substrate, with a very high solid-liquid interface velocity. The final quality of the device is strongly dependent on the phase transformation process which must be controlled extremely carefully in order to achieve polycrystals of sufficient quality and size distribution.

In this work, we have investigated the excimer laser induced crystallization of amorphous Si films on SiO₂ using the large area (~ 50 cm²) XeCl source from SOPRA (model VEL), which delivers pulses of 150 to 200 nsec in duration. The surface melt dynamics was simulated by solving the one-dimensional heat flow equation and the microstructural analysis of the laser irradiated area, for incident energy densities corresponding to the complete melting of the Si layer was demonstrated to be consistent with the SLG regime, firstly reported by Im et al [1], working with a 30 nsec duration excimer laser pulse.

[1] J.S. Im and H.J. Kim, Appl. Phys. Lett. 63 (1993) 1969.

E-II.7 17:50-18:10

APPLICABILITY OF RAMAN SCATTERING FOR THE CHARACTERIZATION OF NANO-CRYSTALLINE SILICON, S. Veprek, Ch. Ossadnik, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, 85747 Garching, Germany and I. Gregora, Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 18040 Prague 8, Czech Republic

In 1980 Veprek et al. reported on the frequency shift of Raman spectra in nc-Si and attributed it to the phonon localization within the quasi-isolated crystallites. Nowadays, Raman scattering is being used as a standard technique for the determination of crystallite size, its distribution and the fraction of the crystalline Si in films consisting of a mixture of nc-Si and a-Si. However, already in our early work we have shown and emphasized that the Raman shift and the normalized scattering intensity from nc-Si depends not only on the crystallite size but also on mechanical stress in the material which may even dominate the observed phenomena. In the present paper we shall briefly summarize these results and present new, systematic study of the effect of the crystallite size and mechanical stress on the phenomena observed in Raman scattering. These results will clearly show that Raman scattering alone cannot provide any unambiguous information regarding the crystallite size, its distribution and crystalline fraction unless additional information regarding the structure and mechanical stress of the films are obtained by other techniques. These results will also show the limits of the accuracy of such measurements.

E-II.8 18:10-18:30

STABILITY AND TRANSPORT PROPERTIES OF MICROCRYSTALLINE Si_{1-x}Ge_x FILMS, F. Edelman, T. Raz, Y. Komem, Materials Engineering Faculty, Technion, 32000 Haifa, Israel, M. Stolzer, Martin-Luther-Universität, Halle (Saale), Germany, P. Werner, Max-Planck-Institut für Mikrostrukturphysik, Halle (Saale), Germany, P. Zaumseil, H.-J. Osten, J. Griesche, Institut für Halbleiterphysik, Frankfurt (Oder), Germany, and M. Capitan, ESRF, Grenoble, France

Polycrystalline SiGe films are a prospective candidate for applications in large area electronics (like active matrix LCD), due to their high mobility and low processing thermal budget relatively to polycrystalline Si films.

The crystallization evolution of Boron and Phosphorus amorphous Si_{1-x}Ge_x films (5·10¹⁷ to 5·10²⁰ cm⁻³), deposited on SiO₂/Si(001) substrates by molecular beam in high vacuum at room temperature, was studied by in-situ methods: XRD, TEM and SEM. The amorphous Si_{1-x}Ge_x films where fully crystallized at ~600°C. Up to 800°C no morphology changes were observed. Between 800 to 950°C, voids and hillocks were gradually developed in the films, which consequently collapsed.

The Hall concentration, mobility and Seebeck coefficient were characterized in the stable Si_{1-x}Ge_x films, annealed between 500 and 800°C. The result showed high mobility and conductivity at room temperature i.g.: 60cm²/Vsec and 2000 Ohm cm⁻¹, respectively, for p-Si_{0.5}Ge_{0.5}.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION III - Thin-Film Transistors

Chairperson: I. French, Philips Research Laboratories, Redhill, UK

- E-III.1** 14:00-14:40 - Invited - **LASER CRYSTALLISED POLY-Si TFTs FOR AMLCDs, S.D Brotherton, J.R. Ayres, M.J. Edwards, C.A Fisher, J.P. Gowers, D.J. McCulloch, M. Trainor, Philips Research Laboratories, Redhill, Surrey RH1 5HA, UK**
The technology for the fabrication of poly-Si TFTs on glass substrates has now reached a level of maturity such that the commercial development of poly-Si AMLCDs is beginning in the Far East. The available technologies will be briefly reviewed and the reasons for the preferred use of excimer laser crystallisation will be summarised. However, there are a number of issues relating to the physics and technology of the TFTs, such as leakage currents, stability and device architecture which need to be addressed, over and above those specific to the details of the laser crystallisation process itself. Some of these issues will be reviewed in this talk, including the role of the incident laser energy density in fabricating high performance TFTs and its dependence on film thickness.
The issues discussed above have determined our design and fabrication of poly-Si AMLCDs and the results obtained from a 2 inch array, with full drive circuit integration, will be illustrated.
- E-III.2** 14:40-15:00 **TFT ANNEALING WITH EXCIMER LASER - TECHNOLOGY AND MARKET OUTLOOK, W. Staudt, S. Borneis, K-D. Pippert, Lambda Physik GmbH, Hans-Böckler-Str. 12, 37079 Göttingen, Germany**
TFT flat panel displays are rapidly increasing their share in the display market by more than 20% per year. Making it one of the fastest growing markets in today's information technology.
Polycrystalline-silicon TFT technology is opening the door to highly reliable, high-resolution, high-performance LCDs that are inevitable for HDTV and advanced multi-media applications.
For the formation of polycrystalline silicon, Excimer laser annealing has shown to be superior to other techniques as far as quality, reliability and economy is concerned. In Excimer laser annealing a high-power laser beam is scanned across the surface of the substrate, coated with amorphous silicon. The silicon is heated up within a few nanoseconds, melts and re-crystallizes into polycrystalline silicon. The substrate remains hereby unaffected. The pronounced non-linearity of the annealing process, the high quality requirements and the high process speeds in the production lines put strong demands on the laser parameters such as energy stability, beam uniformity and stability of output power. During the last two years Excimer laser TFT annealing technology has moved out from the research and development laboratories to real production floors of all main display manufacturers. The first displays manufactured in mass production lines are available on the market. This presentation will discuss the benefits of the recent developments in Excimer laser for TFT annealing, and their impact on the LCD market.
- E-III.3** 15:00-15:20 **TEMPERATURE ANALYSIS OF POLYSILICON THIN-FILM TRANSISTORS MADE BY EXCIMER LASER CRYSTALLIZATION, V. Foglietti, L. Mariucci and G. Fortunato, IESS-CNR, Via Cineto Romano 42, 00156 Roma, Italy**
The recent introduction of excimer laser crystallization (ELC) has led to a tremendous improvement of the polysilicon thin-film transistors (TFTs) performances. In fact, field effect mobilities $> 100 \text{ cm}^2/\text{Vs}$ have been reported, allowing the integration of polysilicon TFTs driving circuits in active matrix LCDs.
In the present work we analysed the electrical characteristics of polysilicon TFTs made by ELC, showing field effect mobilities up to $350 \text{ cm}^2/\text{Vs}$ at room temperature. By using measurements at different temperatures [1] we deduced the density of defects of ELC-polysilicon. The threshold voltage, V_{th} , increases monotonically for decreasing temperature, in agreement with the model that associates V_{th} with the condition of equal trapped and free charge density at the insulator/semiconductor interface. By using the DOS deduced by the "temperature method" [1], a very good agreement between the predicted and experimental V_{th} has been found. Furthermore, we observed a maximum for the field effect mobility around 170 K, that we attribute, similarly to c-Si MOSFETs, to the increasing thermal scattering occurring at higher temperatures and to the scattering with defects, predominant at low-temperatures.
[1] G. Fortunato et al., Philos. Mag. B, vol. 57, p. 573 (1988).
- E-III.4** 15:20-15:40 **COPLANAR AMORPHOUS SILICON THIN FILM TRANSISTOR FABRICATED BY INDUCTIVELY-COUPLED PLASMA CVD, Sung Ki Kim, Se Il Cho, Young Jin Choi, Kyu Sik Cho and Jin Jang, Departments of Physics, Kyung Hee University, Dongdaemoon-ku, Seoul, 13-701, Korea; S.M. Pietruszko, Warsaw University of Technology, IMiO PW, Koszykowa 75, 00-662 Warsaw, Poland**
The electrical and optical properties of the a-Si:H films deposited by inductively-coupled plasma (ICP) chemical vapor deposition (CVD) have been investigated. The ICP-CVD a-Si:H films deposited at 30 mTorr exhibited the hydrogen content of 17 at.%, photosensitivity at 100 mW/cm^2 of 10^6 , activation energy of 0.9 eV.
A novel coplanar self-aligned a-Si:H thin film transistor has been fabricated using Ni-silicide gate and source/drain electrodes. The simultaneous Ni-silicide formation of gate and source/drain regions using the stacked layers of the a-Si:H/SiN_x/a-Si:H reduces the offset length between gate and source/drain about 0.1 μm , which leads to the coplanar a-Si:H TFT. The fabricated self-aligned a-Si:H TFT exhibited a field effect mobility of $0.6 \text{ cm}^2/\text{Vs}$, threshold voltage of 2.3 V, subthreshold slope of 0.5 V/dec. The coplanar a-Si:H TFT can reduce the parasitic resistance down to $5 \times 10^3 \Omega$, on the other hand, the resistance for staggered a-Si:H has higher than $5 \times 10^4 \Omega$ because of the parasitic resistance of a-Si:H between source/drain n-contact and channel. Also, the effect of H₂ dilution for a-Si:H deposition on the coplanar a-Si:H TFT performance has been investigated.

SYMPOSIUM E

E-III.5 15:40-16:00

ION IMPLANTATION OF MICROCRYSTALLINE SILICON FOR LOW PROCESS TEMPERATURE TOP GATE TFTs, Y. Chu, H. Silva, INESC, Lisboa, Portugal; L. Redondo, C. Jesus, M.F. Silva, J.C. Soares, ITN, Sacavém, Portugal, and J.P. Conde, Department of Materials Engineering, Instituto Superior Técnico, Lisboa, Portugal
Amorphous silicon TFTs are usually prepared using a bottom-gate structure. Due to the difficulty in nucleating the Si crystals immediately over the dielectric, bottom gate TFTs using microcrystalline silicon deposited at low substrate temperature (below 350 °C) show inferior electronic properties. One way to avoid this problem is to use a top gate structure with the source and drain contacts prepared by ion implantation. In this paper, ion implantation of phosphorous is used to dope microcrystalline silicon n-type. The microcrystalline silicon is prepared by RF glow discharge and Hot-wire CVD at substrate temperatures between 200 and 350 °C from silane using hydrogen dilution. The implantation is performed at temperatures between room-temperature and the microcrystalline silicon deposition temperature. Isochronal annealing between 200°C and 350 °C is performed to remove the defects induced by the implantation and to activate the dopants. The effect of the implanted dose, implantation energy, implantation temperature, annealing temperature and annealing time on the dark conductivity, activation energy and photoconductivity will be studied. Preliminary studies of the use of these n⁺ layers as contact layers in self-aligned top-gate TFTs are presented. These devices have a microcrystalline active layer and are prepared on Corning glass substrates using a maximum process temperature of 350 °C.

E-III.6 16:00-16:20

ELECTRONIC PROPERTIES OF BOTTOM GATE SILICON NITRIDE/HYDROGENATED AMORPHOUS SILICON STRUCTURES, J.P. Kleider, C. Longeaud, and F. Dayoub, L.G.E.P.- E.S.E. (CNRS,URA 127), Plateau de Moulon, 91192 Gif sur Yvette Cedex, France

Electronic properties of SiN_x/a-Si:H interfaces are studied with complementary techniques. Quasistatic capacitance measurements were achieved on c-Si/SiN_x/a-Si:H/Al MIS structures. Dark Conductivity (DC), Steady-State Photo-Conductivity (SSPC) and Modulated Photocurrent (MPC) experiments were performed on glass/a-Si:H and glass/SiN_x/a-Si:H samples fitted with two coplanar Al electrodes, using the same SiN_x and a-Si:H layers as in the MIS structures.

Results of bias annealing experiments on the MIS structures are explained in the framework of the defect-pool model taking account of a fixed positive charge in the insulator, giving rise to a small band bending in the a-Si:H close to the SiN_x/a-Si:H interface under zero bias equilibrium conditions. This band bending corresponds to a slight accumulation of electrons at this interface clearly put into evidence from the experiments carried out on the coplanar samples. Indeed, we observe that both DC and SSPC are higher if the a-Si:H is deposited on top of the SiN_x layer, the DC activation energy decreasing from 0.75 eV to 0.55 eV. From the MPC measurements, we observe a decrease of the density of states above the Fermi level.

16:20-17:00

BREAK

POSTER SESSION I

17:00-19:00

See programme of this poster session p. E-14 to p. E-19.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION IV - Large Area Sensors and Other Devices

Chairperson: T.Kalfass, Labor für Bildschirntechnik Institut für Netzwerk und Systemtheorie,
Universität Stuttgart, Stuttgart, Germany

- E-IV.1** 8:30- 9:10 - Invited - **LARGE AERA X-RAY DETECTORS BASED ON AMORPHOUS SILICON TECHNOLOGY, J.P. Moy**, Trixell, ZI Centr'Alp, 460 rue de Pommarin, 38430 Moirans, France
- In the last two years, several major manufacturers of medical X-ray imaging equipment have announced new digital imagers for static imaging (radiography) as well as for dynamic applications (fluoroscopy). In medical x-ray imaging, the size of the imager is a deciding criterion. Typically, a general purpose imager must cover at least the chest format, i.e. 35x43 cm. Amorphous silicon was the technology of choice to meet this challenging requirement.
- The basic features of a medical X-ray detector for radiography can be summarized as follows :
- 40 x 40 cm sensitive area composed of $\approx 150\mu\text{m}$ pixels
 - equivalent input noise of a few X-ray photons (@50 keV)
 - dynamic range of the order of 5000:1
 - readout time : 1-5 seconds
- For fluoroscopy, the constraints are even more stringent, as the dose is much lower, corresponding to ≈ 10 X-ray quanta/pixel, and readout should permit 30 frames/s or more.
- Two concepts have led to working devices :
- . 2D arrays of light sensitive pixels optically coupled to a scintillator layer: Fiber structured CsI combine excellent stopping power, X-ray to visible light conversion efficiency and low lateral dispersion of light to maintain a good MTF. CsI:Tl can be grown on top of the array. It matches very well the spectral response of a-Si photodiodes. The sensitive element of the pixel is usually a nip photodiode, 0.5 to 1 μm thick to match the Cs:Tl emission spectrum. The signal is temporarily stored on a capacitance, and sent to charge amplifiers through the column electrodes by means of switching devices controlled by the line voltage. The switching device is either a small diode or a Thin Film Transistor. TFTs are preferred for fluoroscopic applications, as they are faster than the double diode pixel.
 - . 2D arrays of charge collecting electrodes electrically coupled to a photoconductive layer. Amorphous selenium has good transport properties which makes it possible to collect charges across up to a millimetre, a very high dark resistivity and can be deposited in homogeneous thick layers. Charges generated by the absorption of X-rays are collected by simple electrodes, stored on their capacitance and transferred to the column amplifier by TFT switches. The a-Si array is thus less difficult to manufacture, and quite similar to an active matrix LCD panel.
- The conversion from X-rays to electrons is not an efficient process in Se, so that the final number of electrons per X quantum is similar to the number obtained with CsI and photodiodes. The collection of charges by an electric field is not disturbed by scattering, which results in a quasi-perfect MTF. This is obviously beneficial to the sharpness of the image, but also results in noise aliasing which impairs the signal to noise ratio.
- In both cases the realisation of the a-Si plate is a real challenge. Electro-optical properties are critical, and the acceptable defect rate is extremely low : typically no dead line or column in 3k x 3k arrays covering 1000cm²! Several products are now coming into production for both static and dynamic applications, and operation in hospital equipments will start next year. This will be the largest and by far the most complex electro-optical component to date.
- E-IV.2** 9:10- 9:30 **CHARACTERISTICS OF A LINEAR ARRAY OF a-Si:H THIN FILM POSITION SENSITIVE DETECTORS, E. Fortunato**, F. Soares and R. Martins, DCM/FCT-UNL and CEMOP-UNINOVA, Quinta da Torre, 2825 Monte de Caparica, Portugal
- Then increase demand in automation processes in finishing techniques also calls for an automation in the methods of measuring and inspection. These methods ought to be installed as close as possible to the production process as possible and they ought to measure the values needed in a safe and fast way, without disturbing the process itself. Simultaneously they should be free of wear and insensitive against mechanical perturbations. This required approach can be achieved through optical methods of measurement and control, such as by using the proper combination of an array of linear position sensitive detectors and a laser source, able to generate a pattern line to be projected over the object to be inspected.
- The aim of this paper is to present the experimental results of the performances exhibited by such array constituted by 128 elements whose information is processed by a proper analogue/digital converter (MX4), directly coupled to the array and whose information is computer processed, concerning the recognition of patterns and to hold/to process the information collected over the object to be inspected.

E-IV.3 9:30- 9:50

DESIGN ISSUES OF TWO-DIMENSIONAL AMORPHOUS SILICON POSITION-SENSITIVE DETECTORS, Jia-Yi Shung, Klaus Y.-J. Hsu, National Tsing Hua Univ., Dept. of Electrical Eng., Hsinchu, Taiwan, ROC; Yeu-Long Jiang, National Chung Hsin Univ., Dept. of Electrical Eng., Taichung, Taiwan, ROC; Cho-Jen Tsai, National Chung Hsin Univ., Inst. of Materials Eng., Taichung, Taiwan, ROC

Two-dimensional amorphous silicon position-sensitive detector (PSD) is usually in the form of large-area, continuous p-i-n silicon layer structure coupled with resistive layers next to the p and n layers. The device has many applications (e.g. light position measurements, light-pen input devices, etc.) and can be fabricated by using low-cost PECVD process. When used as a light-pen based input device, several material-related design issues must be critically considered for achieving acceptable performance. The present work addresses three important issues, namely the spectral response of PSD, the uniformity requirement of the resistive layers, and the design of optical filter on the input side of PSD, which correspond to the signal-to-noise ratio of the device, the accuracy of light-position determination, and the integration problem with liquid crystal display (LCD), respectively. Analytical analysis and computer simulation results draw the following important conclusions: 1. Red-light-sensitive PSD can be obtained by properly tune the thickness of p and i layers, which suppresses the interference of background light when using the input device under sun light or similar illumination. 2. The spot size of input light has little effect on position determination, as long as the size does not differ too much from that of required resolution. And a conservative uniformity requirement for the resistive layers can be obtained as

$|\Delta h / h| < 4 / n$ with n being the required number of pixels of display. 3. Multi-layered filters made of oxides can be deposited on PSD to reflect non-signal light for LCD display while preserving the input-signal when the PSD is placed under a TN LCD.

E-IV.4 9:50-10:10

STABILITY AND QUANTUM EFFICIENCY OF A NOVEL TYPE OF a-Si:H/a-SiC:H BASED UV DETECTOR, P. Mandracci, F. Giorgis, F. Giuliani, INFN and Dept. of Physics, Polytechnic of Turin, C.so Duca degli Abruzzi 24, 10129 Torino, Italy and M.L. Rastello, IEN Galileo Ferraris, C.so Massimo D'Azeglio 42, 10135 Torino, Italy

We have investigated detectors based on p-i-n a-Si:H/a-SiC:H junctions with high selectivity in the UV region and high stability, deposited by PECVD on substrates of 100 cm² area. The i-type and n-type layers were high electronic quality a-Si:H films, while p-type layers were a-SiC:H films. Thickness of doped layers was fixed to 20 nm, while thickness of the intrinsic layers was varied from 20 to 100 nm. The devices showed a good selectivity with quantum efficiency values of 0.6 for UVA radiation at 365 nm and of 0.15 to 0.03 for visible radiation in the range 400 nm to 650 nm. The stability of the devices was investigated by irradiating the photodetectors with 2000 Joules of UVA radiation: a variation in responsivity lower than 10% was observed. Correlations between a-Si:H material properties and stability at UV irradiation and device performances were investigated by monitoring optical and electrical properties and defects in films with thickness varying from 20 to 1000 nm.

E-IV.5 10:10-10:30

Al-BASED SPUTTER-DEPOSITED FILMS FOR LARGE LIQUID-CRYSTAL-DISPLAY SUBSTRATES, H. Takatsuji, T. Arai and S. Tsuji, Display Technology, IBM Japan, Ltd., Shimotsuruma, Yamato-shi, Kanagawa 242, Japan; K. Kuroda and H. Saka, Department of Quantum Engineering, Nagoya University, Nagoya 464-01, Japan

Aluminum-based alloys are expected to be increasingly used for wiring on high-performance thin-film-transistor (TFT) arrays formed on glass substrates due to their low resistivity. However, Al is prone to both hillock formation and whisker growth, which are among the major yield detractors during TFT device fabrication. It is well known that the resistance to stress migration is related to a film's nanostructure.

In this work, the relationship of the nanostructure of the various sputtered Al films on the LCD-grade large glass substrates (550 X 650 mm), the sputtering apparatus, and their parameters is investigated by the Taguchi method [1]. We demonstrate a method of controlling the film nanostructure for Al and Al-based alloy wiring on TFT-LCD arrays. The film nanostructure is analyzed by atomic force microscopy (AFM), X-ray diffraction (XRD), and cross-sectional transmission electron microscopy (TEM), while the resistance to hillock and whisker generation is investigated by means of our nano-indentation techniques [2]. Some Al and Al-based alloy wiring structures for TFT arrays are also presented.

[1] "Quality control, robust design, and the Taguchi method", K. Dehnad, Brooks/Cole Pub. Co., Pacific Grove, CA 1989

[2] H. Takatsuji, et al., Mater.Res.Soc.Proc. Vol. 441, pp. 415-420

10:30-10:50

BREAK

E-IV.6 10:50-11:30 - Invited -

LOW TEMPERATURE SILICON DEPOSITION FOR LARGE AREA SENSORS AND SOLAR CELLS, M.B Schubert, Univ. Stuttgart, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, Germany

Materials research has paved the road for the rapidly growing application of amorphous silicon (a-Si:H) thin film devices like transistors for active matrix addressing or double- and triple-stacked solar cells. The performance of these devices, however, is limited due to poor electronic transport. Therefore many researchers try to take advantage of the superior electronic quality of crystalline silicon (c-Si) for large area devices. These efforts of combining the benefits of low and high temperature technologies can be grouped into three main areas: i) development of large area c-Si on glass by high rate thin film deposition; ii) design of hybrid systems by adding functionality to ready-made microelectronics circuits; and iii) invention of completely new systems and devices on flexible substrates like steel or plastic foils. The first attempt includes techniques like very high frequency (VHF) plasma enhanced chemical vapour deposition (PECVD), hot-wire deposition and laser crystallisation; the second one enhances sensor capabilities for image processing and gas detection; and the third one just starts with organic light emitting diodes, TFTs on steel, smart cards etc. This presentation will review own work in all three areas, discussing device problems as well as more fundamental aspects of deposition technology and manufacturing. Hot-wire deposition and VHF PECVD yield similar quality nanocrystalline silicon, but also post-deposition changes have to be considered. Two-terminal a-Si:H colour sensors and photodiodes for retina implantation demonstrate the potential of hybrid microsystems, and the solutions obtained there will form our toolbox for novel large area devices.

SYMPOSIUM E

E-IV.7 11:30-11:50

DEVICE-QUALITY POLYCRYSTALLINE SILICON FILMS DEVELOPED AT LOW PROCESS TEMPERATURES BY HOT WIRE CHEMICAL VAPOR DEPOSITION, S.C. Saha, J. Guillet, S. Hamma, J.E. Bourée, Laboratoire de Physique des Interfaces et des Couches Minces, CNRS UPR 0258, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Device-grade undoped polycrystalline silicon thin films have been developed from a gas mixture of silane and hydrogen using a hot wire chemical vapor deposition (HW-CVD) method, optimizing the deposition parameters. Proper design of the HW-CVD reactor helps to deposit a uniform quality of film over a large area (100cm²) with two filaments configuration. Extensive studies have been made on the effects of hydrogen dilution (4-60), substrate temperature (180-400°C) and filament temperature (1500-1700°C) on the growth of the films. AFM micrographs give a quantitative estimate of roughness of these films. UV-visible ellipsometry analyses confirm their compactness and crystallinity while X-ray diffraction patterns allow for the determination of the crystallite sizes (up to 400 Å). At a substrate temperature of 300°C and a filament temperature of 1500°C, using a hydrogen dilution of 60, a dark conductivity of $2.5 \times 10^{-5} \text{ S cm}^{-1}$ and its activation energy of 0.45 eV have been obtained. For these films, the Hall mobility attains $80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These films can be utilized as active layers in thin film transistors and thin film solar cells realized by HW-CVD at the low process temperatures on large area glass substrates.

E-IV.8 11:50-12:10

FEMTOSECOND DIAGNOSTICS OF Si(001)-BASED MOS STRUCTURES BY PHOTOINDUCED AND DC-ELECTRIC FIELD INDUCED SECOND HARMONIC GENERATION, M. Anderson, P. Wilson, and M.C. Downer, Physics Department, The University of Texas at Austin, Austin TX 78712, USA, M.L. Lyubimova, E.D. Mishina, and O.A. Aktsipetrov, Department of Physics, Moscow State University, Moscow 119899, Russia

Photoinduced effects in DC-electric field induced second harmonic generation (EFISH) are studied experimentally and theoretically in Si-SiO₂-Cr MOS structures at the subpicosecond time scale that gives the means of MOS structure diagnostics. The size of the silicon wafer up to 300 mm does not restrict the potentialities of the techniques suggested.

Experimental EFISH studies are performed using pump-probe configuration and photomodulation technique, for which two beams of the splitted output of a tunable femtosecond Ti-Sapphire laser are used as a pump and probe radiation. The pump beam generates electron-hole pairs in conduction band of subsurface Si layers, whose injection changed the space charge region parameters of the MOS structure. The probe beam generates the second harmonic radiation from the silicon subsurface regions with photomodified parameters. Photomodulation efficiency depends on applied bias and photon energy and allows one to measure the local (with the spatial resolution about several microns) parameters of MOS structure: silicon doping concentration, interface trap concentration and the surface recombination constant.

E-IV.9 12:10-12:30

Ge:Si:O EVAPORATED ALLOYS AS THERMOSENSITIVE LAYER FOR LARGE AREA BOLOMETERS, E. Iborra, J. Sangrador, M. Clement, Dto. Tecnología Electrónica, Universidad Politécnica de Madrid, 28040 Madrid, Spain and J. Perriere, Groupe de Physique des Solides, Université de Paris VII, 2 place Jussieu, 75251 Paris, France

Amorphous germanium doped with oxygen has been widely used as thermosensitive material in large area bolometers for X-ray or IR detection. The addition of silicon in this compound is expected to improve the thermal sensitivity of the material by increasing the temperature coefficient of the electrical resistivity while keeping its electrical resistivity moderately low. This work presents a study of the amorphous Ge:Si:O thin films deposited at low temperature in a coevaporation system. Films with various compositions are obtained by controlling separately the evaporation rates of germanium and silicon, the oxygen pressure and the substrate temperature. Films with silicon to germanium rate from 0 to 0.4 and oxygen contents up to 25% atomic are analysed. The films are characterized by RBS, NRA, FTIR, EDX and temperature behaviour of the electrical resistance. The analysis of all experimental data shows that oxygen incorporation depends on silicon contents in the films and substrate temperature, but not on oxygen pressure. Oxygen is found to be bonded to silicon but not to germanium. Nevertheless, an uniformed distribution rather than a cluster structure of silicon oxide into a germanium matrix is suggested. Preliminary studies of thin films with similar compositions obtained using reactive sputtering from a composite target evince the coexistence of Si-O and Ge-O bonds homogeneously distributed.

12:30-14:00

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION V - Field Emission and EL Displays

Chairperson: G. Fortunato, DCM/FCT-UNL and CEMOP-UNINOVA, Monte de Caparica, Portugal

- E-V.1** 14:00-14:40 - Invited - **LARGE AERA FIELD EMISSION DISPLAYS, J.E. Jaskie**, Motorola, Advanced Display Technologies, Phoenix Corporate research Laboratories, 2100 East Elliot Road, Tempe, Arizona 85284, USA
- For many years one of the goals of the consumer electronics industry has been the development of a flat CRT. The performance of CRTs are still the standard against which all displays are measured. The major disadvantage to their use is the mechanical structure that is bulky and unwieldy for portable use, and large and heavy for large area displays. After many years of development, Field Emission Displays that are essentially flat CRTs, and that use conventional Spindt tip geometries, are becoming an industrial reality. Engineering evaluation displays are now available and several companies around the world are currently building production facilities. The future evolution of Field Emission Displays will be towards low work function electron emitters that offer improved performance and lower cost for larger size displays. Diamond-Like Carbon (DLC), or amorphous carbon, has been demonstrated in laboratories to show attractive combinations of robustness and low effective barrier to electron emission. The ease with which this material can be deposited over large areas promises to enable large area flat panel displays that will be only a few millimeters thick. However, there are many puzzles in the behavior of this material that are still poorly understood. The status of Field Emission Displays, Carbon emitters, and their potential for Large Area Field Emission Displays will be discussed.
- E-V.2** 14:40-15:00 **ENHANCING THE FIELD EMISSION PROPERTIES OF AMORPHOUS CARBON FILMS BY THERMAL ANNEALING, A.P. Burden, R.D. Forrest, and S.R.P. Silva**, School of Electronic Engineering, Information Technology & Mathematics, University of Surrey, Guildford, GU2 5XH, UK
- Polymeric hydrogenated and nitrogenated amorphous carbon films (a-C:H:N) have been deposited on silicon substrates using a Plasma Technology DP800 radio frequency Plasma Enhanced Chemical Vapour Deposition system. This equipment was configured with an earthed water-cooled substrate table, allowing the carbon film to grow under low bias conditions at a rate of 2-3 Å s⁻¹, yielding a film with a refractive index of ~1.5-1.7, and an E_{opt} optical band-gap of ~3-4 eV, depending on the growth parameters employed. The field emission properties of these films have been studied using a sphere-to-plane anode-cathode configuration, and the dependence of film thickness and nitrogen content investigated. A significant lowering of the emission threshold field has been measured after treating the films for 1800 s at 400°C and this has been correlated with a simultaneous study of the change in the films' microstructural properties. We conclude that the changes commensurate with the onset of graphitisation are beneficial for field emission, and that the associated improvements in the films' mechanical stability will aid incorporation into large-area displays. Field emission from thermally stressed films below the treatment temperature are also characterised with a view to producing cathodes suitable for high temperature operation.
- E-V.3** 15:00-15:20 **INFLUENCE OF SURFACE MORPHOLOGY OF THE POLYCRYSTALLINE SILICON ON FIELD ELECTRON EMISSION, A.A. Evtukh**, Institute of Semiconductor Physics, 45 Prospekt Nauki, Kiev 252650, Ukraine
- Electron field emission from polycrystalline silicon have been investigated. The polycrystalline silicon was deposited by LP CVD. Polysilicon layer was then diffusion doped with POCl₃ at 950°C for 30 min. Sharpening of asperities on polysilicon layer surface was performed by thermal oxidation in dry O₂ or H₂O at different temperatures in the range 900-1000°C. After oxidation and removing the oxide the surface of polycrystalline silicon have developed asperities, especially in case of oxidation at lower temperature. The asperities on polysilicon surfaces have special irregularities, i.e. different sizes (height - base ratio) and shapes. The surface morphology was estimated by scanning electron microscope (SEM). The measurement of emission current from samples were performed in high vacuum system, which could be pumped to stable pressure 10⁻⁶ Torr. The emission areas and local field enhancement factors have been determined and used during explanation relationship among current - voltage curves for polycrystalline silicon with different surface morphology. The polycrystalline silicon layer characterized relatively high emission current. This is connected with large emission area. The changing of surface morphology allows to rule the emission current sufficiently.
- E-V.4** 15:20-15:40 **VISIBLE PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE FROM Si NANOCRYSTALLINE THIN FILMS, Wei Wu, X.F. Huang, K.J. Chen**, Department of Physics, Nanjing University, Nanjing 210093, China; J.B. Xu, Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong
- We report the fabrication of nano-Si crystallites by excimer laser annealing of the amorphous Si/SiN_x multilayers. Visible photoluminescence (PL) and electroluminescence (EL) were observed at room temperature with a-Si:H well layer thickness narrower than 4.0 nm. PL spectrum shows a peak wavelength around 640 nm, while EL spectra exhibited two peaks positioned at the wavelengths from 600 nm to 750 nm. It is clear shown the irradiation energy densities and amorphous Si layer thickness play important role in the luminescent characteristics. With decreasing the a-Si:H well layer thickness, significant blue-shift of the EL peak was observed. In comparison with the model of theoretical computing, and the size of Si crystallites, the visible luminescent phenomena are interpreted as the combined result of radiative recombination via silicon quantum well states and hydrogen related species.

SYMPOSIUM E

- E-V.5** 15:40-16:20 - Invited - **FROM MATERIALS TO PRODUCTS: A SYSTEM PERSPECTIVE, C. Reita,**
Thomson-CSF, Laboratoire Central de Recherche, Domaine de Corbeville, 91404 Orsay
Cedex, France
- Large area microelectronics has moved, in the last ten years, from the laboratory demonstrator stage to a multi-billion dollars industry. Products like Active Matrix Liquid Crystal Displays (AMLCDs) and large area sensors are now widely available and range in size from about 1 to 21 inches. This has been accomplished thanks to a continuous improvement in material properties and in fabrication technology, although the transfer, from the laboratory to the factory has not always been a direct process. The reason reside mostly in the fact that material scientists (like everybody else) tend to focus on the primary object of their work, and to forget that a material this is just a building block to produce a working and reliable system. Moreover, the system has to be produced at a price and in quantities such to be able to make a reasonable profit out of it. In this paper the issues of material properties and manufacturability for large area electronic systems will be discussed from the standpoint of the system designer.
- The most important issue is probably the effect of the materials characteristics on the devices performance. Intrinsic properties of materials themselves, like fixed charges in insulators, gap density of states in active materials, textures and surfaces, as well as their interaction when put together in a device, affect in a complicated way the electrical characteristics of devices and circuits. Some of these effects in the case of TFTs will be shown with the aid of simulations and experimental data. It emerges that the optimisation process of a material cannot be separated by the optimisation of the device as a whole, and performed without a clear understanding of the system in which it will be used.
- Another issue that will also be addressed is the manufacturability of the system. The requirement of process tolerance and uniformity is often neglected in the first stages of the study of a material, but is of a paramount importance when systems have to be fabricated on a large scale. Again with the aid of circuit simulations, it will be shown how compromises have to be done in the design phases to allow for non-uniformity and how important the process control can be.
- The lesson to be taken is that the final application of the materials has to be taken into account from the earliest possible stages of the study, and that circuit designers and process engineers have to be involved in the material research to reach the market in the shortest possible time with the best possible products.

16:20-17:00

BREAK

POSTER SESSION II

17:00-19:00

See programme of this poster session p. E-20 to p. E-24.

END OF SYMPOSIUM E

SYMPOSIUM E

SYMPOSIUM E
POSTER SESSIONS

Wednesday June 17, 1998
Mercredi 17 juin 1998

Afternoon
Après-midi

Poster Session I
17:00-19:00

- E-I/P1** **DEPOSITION FILMS a-Si:H IN COMBINED (LF+HF) DISCHARGE**, D.I. Grunsky, M.N. Bosyakov, A.P. Dostanko, D.V. Juk, Belarussian State University of Informatics and Radioelectronics, P. Brovka Street, 220027 Minsk, Belarus
Experiments on investigation of two-frequency (55kHz+13.5mHz) discharge were carried out. Two-frequency discharge was formed by combination of HF or LF voltage. Investigations were made in two directions: varied HF power was added to basic LF discharge and vice versa. The deposition rate was increased by 100% while adding LF (variable) power to HF-discharge (basic mode) and was increased by 35% while adding HF (variable) power to LF-discharge (basic mode). Obtained films had a "device quality".
Optical band gap (Eg) in a-Si:H films can be changed by varying addition power. For instance, in basic HF discharge Eg=1.91 eV, but by adding LF power Eg=1.77. On the other hand by adding HF power on basic LF discharge optical band gap increased with 1.69 to 1.77 eV.
- E-I/P2** **DEPOSITION OF NANOCRYSTALLINE SILICON ON ULTRA THIN ALUMINUM UNDERLAYERS BY PCVD AND SPUTTER-DEPOSITION AT 500K**, T.P. Drüsedau, A. Diez and J. Bläsing, Otto-von-Guericke-Universität, Institut für Experimentelle Physik, PF 4120, 39016 Magdeburg, Germany
Double layers of the type Al/Si were prepared at 500 K onto silica without breaking the vacuum in a multichamber deposition apparatus and characterized by X-ray methods, SIMS, atomic force and electron microscopy. Al films of a thickness of 4 to 30 nm were prepared by magnetron sputtering (MSP). Si films with a thickness between 100 and 500 nm, which show an amorphous structure in absence of the Al- underlayer, were prepared by either MSP or PCVD at a rate of 0.5µm/h. Depending on the thickness and the preparation condition of the Si and the Al layer, the structure of the upper Si layer can be changed from amorphous to fully crystalline with a maximum crystallite size of about 30 nm. At growth conditions of high energetic input into the growing Si layer (e. g. MSP at low argon pressure), the crystallite formation is strongly suppressed. The major fraction of the Al remains in the underlayer. Crystallite formation is connected with a diffusion of Al into the growing film with typical concentrations in the 100 ppm range, whereas under strong energy flow an Al concentration around 1 ppm is measured within the Si. The aluminum-mediated growth of nc-Si is related to the presence of a metastable aluminum silicide, which has a high diffusivity for Al and Si, causing a bond rearrangement in the Si network.
- E-I/P3** **PREPARATION AND CHARACTERIZATION OF a-Si_{1-x}C_x:H FILMS DEPOSITED IN HELIUM REMOTE PLASMA FROM TRIMETHYLCHLOROSILANE**, T.P. Smirnova, L.V. Yakovkina, B.M. Ayupov, I.P. Dolgovesova, V.A. Nadolinny, V.N. Kitchay, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Dpt., Lavrentjev Ave 3, Novosibirsk, Russia
A hydrogenated silicon-carbon films were produced by excited helium-induced chemical vapour deposition using trimethylchlorosilane as a single-source precursor. The effect of substrate temperature (T_s) on the deposition rate has been investigated. Chemical composition, optical and structural properties were explored using IR-spectroscopy, ellipsometry, X-ray diffractometry and diffractometry of synchrotronous radiation. Excited helium-induced CVD process made it possible to obtain the silicon carbide films from trimethylchlorosilane at T_s≥673K characterising by following properties: the films tend to crystallisation with exhibiting of β-SiC structure; the films are found to be optically homogeneous; their refractive index and optical gap coincide with the values for crystalline silicon carbide (n=2.7, E_g=2.4eV). Defects investigation by the method ESR shows that the paramagnetism of films, obtained at T_s=673K, is caused the broken bonds on carbon. Kinetic studies have displayed that the deposition process is controlled by the desorption of hydrogen from the surface of the growing film.
- E-I/P4** **CARRIER TRANSPORT, STRUCTURE AND ORIENTATION IN POLYCRYSTALLINE SILICON ON GLASS**, K. Nakahata, A. Miida, T. Kamiya, C.M. Fortmann and I. Shimizu, Dept. of Innovative and Engineered Materials, The Graduate School, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
Polycrystalline silicon films were grown on glass from gaseous mixture of SiF₄ and H₂ by HRCVD (Hydrogen Radical-enhanced CVD). In this technique, the structure, i.e., crystallinity, grain size, orientations and grain boundaries, were widely varied by the deposition parameters such as mixing ratio of source gases, substrate temperature.
In this study, we investigated the relationship between the structure and carrier transport properties for the films showing clear textures; (022) and (400) preferential orientation in XRD. Carrier density and Hall mobility were measured at wide temperature range from 100K to 400K by Hall effect using a cell geometry with 6 terminals. The Hall mobility at room temperature increases from 2(cm²/Vs) to 16(cm²/Vs) with an increase in the XRD(022) intensity and with a reduction of the full width at half maximum in Raman spectra for the films of (022) preferential orientation showing high crystallinity (>90%), which implies that the mobility is mainly ruled by the grain size and their structural fluctuation. From the temperature dependence of Hall mobility, a part of carriers (electrons) are considered to pass through the grain boundaries by tunneling at low temperature. On the contrary, rather low Hall mobility was unexpectedly obtained for the films with (400) preferential orientation showing fairly low structural fluctuation. In this film, the point-defects located at the grain boundaries which were not passivated may prevent efficiently the carrier transport. We will discuss on the photoelectric properties of these polycrystalline silicon films.

- E-I/P5** SOLID PHASE CRYSTALLIZATION OF AMORPHOUS SiGe FILMS DEPOSITED BY LPCVD ON SiO₂ AND GLASS, J. Olivares, A. Rodriguez, J. Sangrador, T. Rodriguez. E.T.S.I.T-U.P.M., Madrid, Spain; C. Ballesteros, E.P.S.-U.Carlos III, Leganés, Madrid, Spain; A. Kling. C.F.N.U.L., Lisbon, Portugal

The crystallization kinetics and film microstructure of poly-SiGe layers obtained by solid phase crystallization of amorphous SiGe with Ge fractions appropriate for the fabrication of thin film transistors have been studied in detail. Amorphous SiGe layers were deposited by LPCVD at 450°C on oxidized Si wafers and 7059 Coming glasses, using Si₂H₆ and GeH₄ as gas sources. The films were 100 nm thick and the Ge fraction (x) was in the 0-0.38 range. The samples were annealed at 550°C for times up to 450 h at low pressure (below 100 mTorr) to crystallize the amorphous layers. The crystallization behavior was analyzed by X-ray diffraction and transmission electron microscopy. The experimental results on growth kinetics fit the Avrami's model. The characteristic crystallization time decreases slowly for x<0.3 and more abruptly for higher values of x. The transient time is too short to be determined in the samples with x>0.2. The grain size in the fully crystallized layers is lognormally distributed with an average grain size around 500 nm and a standard deviation around 150 nm. The grains are slightly larger in the layers deposited on glass. The recrystallized films deposited on SiO₂ have a (111) preferred orientation for low values of x and evolve to a randomly oriented polycrystal as x increases. For films deposited on glass, the (111) orientation is maintained for all the values of x studied.

- E-I/P6** POLYCRYSTALLINE SILICON FILM GROWTH IN A SiF₄/SiH₄/H₂ PLASMA, B. Lee, L.J. Quinn, P.T. Baine, S.J.N. Mitchell, B.M. Armstrong and H.S. Gamble, Dept. of Electrical & Electronic Engineering, The Queen's University of Belfast, Belfast BT9 5AH, UK

Low temperature deposition of polysilicon is an attractive technology for the future production of liquid crystal displays, image scanners and large area electronics. The most common ways of producing device quality polysilicon are by solid phase crystallisation or laser annealing of previously deposited amorphous silicon films. This paper reports that it is possible to obtain polysilicon layers with excellent crystallinity from a PECVD process using a SiF₄/SiH₄/H₂ gas mixture. Previous work [1] has indicated that it is possible to achieve crystalline films with grain sizes averaging 400Å. Further optimisation of this process has yielded average grain sizes up to 900Å at 300°C at reasonably high deposition rates. It has been suggested that the use of SiF₄ as a precursor for polysilicon deposition may have an in-situ cleaning effect during deposition leading to improved crystallinity of the layer. It is thought that in such a process, growth and etching may take place simultaneously. This paper investigates the effect of gas flow ratios, rf power and chamber temperature on the deposition rate and the grain sizes of the polysilicon films. The crystallinity of the silicon layers was determined by the use of Atomic Force Microscopy. [1] "Deposition and Characterisation of Silicon grown in SiF₄/SiH₄/H₂ mixture for TFT applications", EMRS 1996, Thin Solid Films Vol.296, pp.7- 10, 1997

- E-I/P7** PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF NANOCRYSTALLINE SILICON FILMS FROM SiF₄-H₂-He AT LOW TEMPERATURE, G. Cicala, P. Capezzuto and G. Bruno, Centro di Studio per la Chimica dei Plasmi, Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy

The growth of micro- (nano)-crystalline silicon, at substrate temperature lower than 300 °C is important for the manufacturing of high-mobility thin film transistors, of large-area active matrix for liquid-crystal display and solar cell and of light emitting devices. Generally, low-temperature plasma enhanced chemical vapor deposition of nc-Si is more difficult because the crystallization is hindered at low temperature by the poor migration of the growth precursors.

We have obtained nc-Si:H(F) by r.f. PECVD starting from SiF₄-H₂ mixtures in which the amorphous-to-nanocrystalline transition is favored because of the presence of F atoms, which preferentially etch the amorphous phase. The He addition to the SiF₄-H₂ gas mixture induces higher crystallinity due to the increase of F and H atoms in the plasma. The improvement of the deposition conditions for the nc-Si:H(F) film structure is carried out by adjusting the r.f. power and the deposition temperature. In presence of He, the deposition temperature for nc-Si:H(F) can be decreased to 120°C reducing the stress and still maintaining a high degree of crystallinity. Optical emission spectroscopy (OES), laser reflectance interferometry (LRI) and mass spectrometry (MS) are employed as in situ plasma phase diagnostic techniques. The F/SiF₂ ratio value is crucial to control the etching-deposition competition and, therefore, the amorphous-to-nanocrystalline transition. The structural and optical properties of the film are determined by X-ray diffraction, by Raman, ellipsometric, Fourier transform infrared spectroscopy and by UV-Vis absorption spectroscopy.

- E-I/P8** TRANSPORT CHARACTERIZATION OF HIGH MOBILITY LOW TEMPERATURE PECVD MICROCRYSTALLINE SILICON, R. Brenot, J.P. Kleider*, C. Longeaud*, T. Mohammed Brahim**, R. Vanderhaghen, Laboratoire de Physique des Interfaces et des Couches Minces, UMR 7647 du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France; *Laboratoire de Genie Electrique de Paris, Ecole Supérieure d'Electricité, 91192 Gif/Yvette Cedex, France; **Laboratoire de Microélectronique et Visualisation, Université Rennes 1, 35042 Rennes Cedex, France

High mobility microcrystalline silicon is deposited at low temperature, on conventional RF (13.56 MHz) PECVD reactor, from H₂ diluted SiF₄ plasma. One may obtain mobility higher than 20 cm²V⁻¹s⁻¹. The carrier transport, transversal and longitudinal, is analyzed, using Time Resolved Microwave Conductivity (TRMC), Hall mobility measurement, Photomodulated Current, Capacitance and Time of Flight. From these various transport characterizations, whose validity is discussed, and their comparison with deposition condition, we modelize the transport mechanism, taking into account amorphous and crystalline contributions.

- E-I/P9** STABILITY OF DIELECTRIC PROPERTIES OF PECVD DEPOSITED CARBON-DOPED SiOF FILMS, J. Lubguban, Jr., Y. Kurata, T. Inokuma, and S. Hasegawa, Faculty of Engineering, Kanazawa University, Kanazawa 920, Japan

Carbon-doped SiOF films were deposited by adding CH₄ to SiH₄/CF₄/O₂ gas mixtures using a plasma-enhanced CVD method. Deposition temperature, rf power and deposition time were fixed at 300°C, 10 watts and 35 min respectively. By adjusting the deposition conditions, SiOF film with a low dielectric constant ε_s of 3.1 can be obtained without CH₄ gas. However, after 7 days, ε_s increased to 3.5 due to instability of the films upon exposure to air. Upon CH₄ addition, the dielectric constant increased in the range of 3.14 to 3.4, but the change in ε_s after 7 days air exposure are not large compared with that for films without CH₄. In particular, at a relatively low CH₄ flow rate, ε_s was significantly low (ε_s = 3.14) and the change in ε_s after 7 days was only 3.17. The result suggests that CH₄ addition acts to enhance the water absorption resistivity of the films. The FT-IR spectra of the films shows a decrease in the density of Si-F bonds with increasing the CH₄ flow rate which may be a reason for the increase in the dielectric constant.

- E-I/P10** HIGH RATE DEPOSITION OF ta-C:H USING AN ECWR PLASMA SOURCE, N.A. Morrison, S. Muhl, S. Rodil, J. Robertson, W.I. Milne, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK and M. Weiler, CCR, Maarweg 5, 53619 Rheinbreitbach, Germany

There are numerous large area applications of diamond-like carbon such as field emission sources, optical coatings for bar-code scanners and tribological coatings for magnetic hard disks. A compact RF electron cyclotron wave resonance (ECWR) plasma reactor has been developed for the high rate plasma deposition of hydrogenated tetrahedral amorphous carbon (ta-C:H). The ECWR is a low pressure plasma source which provides high plasma densities of up to 10¹² cm⁻³, growth rates up to 2 nm/s, a large area facility and independent control of the deposition rate and ion energy. The ta-C:H deposited from acetylene has sp³ fractions up to 65%, and optical gaps up to 2.5 eV. The ta-C:H is further characterised in terms of hydrogen content, surface roughness, C-H bonding, and friction coefficient.

- E-I/P11** MICROSTRUCTURES OF POLYCRYSTALLINE SILICON THIN FILMS PREPARED BY HOT WIRE CHEMICAL VAPOR DEPOSITION WITH HYDROGEN DILUTION, X. Guo, M. Zhu, Graduate School, Academia Sinica, P.O.Box 3908 Beijing, China; B. Dong, Institute of HEP, Academia Sinica, Beijing, China; H. Han, Institute of Semiconductors, Academia Sinica, Beijing 100084, China

Intrinsic polycrystalline silicon thin films, $10^{-3} (\Omega\text{cm})^{-1}$ in conductivity, were prepared by hot wire chemical vapor deposition with a gas mixture of $\text{S} = \text{H}_2/\text{SiH}_4$. Microstructures of the poly-Si films varying with S have been studied by x-ray diffraction, Raman scattering, infrared (IR) and small angle x-ray scattering (SAXS). The initial microcrystalline Si layer, instead of commonly observed amorphous layer, on the glass substrate was observed at $\text{S}=49$ from transmission electron microscopy and back-side injected Raman spectra. Both grain size and the volume fraction of crystalline increase with S. The SAXS indicates that as increasing the S from 1 to 49, the volume fraction of micro-voids is reduced by a factor of 10. The IR spectra show that the C_H as well as bonded H decreases with increasing S. Hydrogen is essentially bonded with silicon in Si-H_2 configuration in poly-Si:H. Combining the data of IR and SAXS, we conclude that the Si-H_2 bonds in poly-Si:H thin film are located at the grain boundaries rather than in the internal surface of the micro-voids of the film.

- E-I/P12** THICKNESS CONTROL AND RECRYSTALLIZATION OF THE AMORPHOUS BUFFER LAYER OF NANO-CRYSTALLINE SILICON, F. Gourbilleau, A. Achiq, P. Voivenel and R. Rizk, LERMAT, unité CNRS 6004, 6 Bd Maréchal Juin, 14050 Caen cedex, France

The promising development of direct deposition at relatively low temperature T_d of hydrogenated nanocrystalline silicon layer for microelectronic applications, is somewhat hindered by the formation of an amorphous buffer layer (ABL) at the substrate-deposit interface. By means of electron microscopy observations and infrared (IR) absorption spectroscopy measurements, the present study shows the dependence of the ABL thickness on the cooperative effects of T_d , the dopant concentration and the deposition duration. While at low T_d ($<100^\circ\text{C}$), this thickness is governed by the present impurities or dopants that act as nucleation sites and then decrease the ABL thickness, the thermal activation of SiH_2 species, identified by IR data, seems to dominate the nucleation and crystallization processes at higher deposition temperatures. Moreover, considering the effect of the deposition duration on the decrease of the ABL thickness, it is demonstrated that a more or less long annealing at the substrate temperature with a turned-off plasma, is able to completely recrystallize the above-mentioned interfacial layer. The thickness of this layer can then be monitored by a judicious adjustment of the deposition temperature, dopant concentration and deposition duration parameters.

- E-I/P13** HYDROGEN PARTIAL PRESSURE EFFECTS ON THE STRUCTURE AND PROPERTIES OF THE SPUTTERED SILICON LAYERS, A. Achiq, R. Rizk, F. Gourbilleau and P. Voivenel, LERMAT, unité CNRS 6004, ISMRA, 6 Bd Maréchal Juin, 14050 Caen cedex, France

Silicon thin films have been deposited by RF sputtering technique using a plasma of argon and hydrogen mixture. The structural, optical and electrical characteristics have been investigated by infrared absorption, Raman scattering, transmission electron microscopy (TEM), optical absorption and dark conductivity, σ_d , measurements, as a function of the hydrogen pressure rate $r_\text{H} = P_\text{H}_2/P_\text{tot}$. For low values of r_H ($\leq 20\%$), the layers were found completely amorphous with an hydrogen content C_H that increases with r_H . By contrast, higher pressure of hydrogen ($r_\text{H} \geq 40\%$) leads to a partial crystallization of the deposit whose crystalline fraction increases up to 74% when r_H reaches 100%, together with a concomitant decrease of C_H . This features is explained by the role of the chemically active SiH_3 radicals. A consistent widening of the optical band gap E_0 and a coherent decrease of σ_d have been noticed as far as C_H increases for the completely amorphous layers. These parameters show, on the contrary, opposite behaviours to those described above, when a partial crystallization starts to take place. A variation of more than 8 orders of magnitude has been revealed by the structural changes of the deposited layers: σ_d evolves from $\sim 10^{-10} \Omega^{-1}\text{cm}^{-1}$ for the most hydrogenated a-Si to near $10^{-2} \Omega^{-1}\text{cm}^{-1}$ for the most crystallized one, where the activation energy decreases to a value as low as 0.13 eV.

- E-I/P14** STABILITY OF LPCVD AMORPHOUS SILICON, A. Sliwinski and S.M. Pietruszko, Warsaw Univ. of Technology, IMiO PW, Koszykowa 75, 00-662 Warsaw, Poland; J. Jang, Dept. of Physics, Kyunghee University, Dongdaemoon-ku, 130-701 Seoul, Korea

The stability of amorphous silicon is very important issue in device performance. We report the study of the influence of dopants (P and B) and H content on transport properties and thermally induced metastability in LPCVD a-Si (thermal decomposition of silane at 560°C). The films were implanted with a P or B doses to achieve concentration from $1 \times 10^{17}/\text{cm}^3$ to $2 \times 10^{21}/\text{cm}^3$, following H implantation (4.5 and 12 at.% of H).

We have found that it is possible to dope LPCVD a-Si with P and B despite high density of spins ($10^{19}/\text{cm}^3$) and low hydrogen content (0.06 at.%) in as-grown material. The σ_RT of as-grown films is $1 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$ and increases to $1 \times 10^{-1} \Omega^{-1}\text{cm}^{-1}$ or $1 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$, P or B doping, respectively. Accordingly E_AI , which is 0.7 eV in as-grown films, decreases to 0.2 and 0.25 eV, respectively. Introducing of H causes decreasing of σ_RT and increasing of E_AI in both kinds of doping. The change in σ_RT is two orders of magnitude for the highest dopant and H concentration. We attribute this reduction in doping efficiency to formation of P-H and B-H complexes.

The thermally induced metastability was observed in unhydrogenated slightly P- or B-doped a-Si films. The equilibration temperature was found to be $300 \pm 20^\circ\text{C}$ for P-doped films, which is higher (about 50°C) than that in B-doped LPCVD a-Si. We have found that T^* decreases (50°C) with the increasing P concentration, however remains constant in case of B doping. Hydrogen decreases T^* for both type of doping, however the change is more pronounced in case of P doping. In the paper, differences in σ_RT and E_AI after slow cooling and quenching presented. The results presented in this work qualitatively agree with the H-glass model.

- E-I/P15** HYDROGENATED AMORPHOUS SILICON THIN FILMS. PREPARATION, STRUCTURAL AND OPTICAL CHARACTERIZATION, A. Chouiyakh, K. Mellassi and K. Benai, University Ibn Tofail, Faculty of Science, Department of Physics, B.P.133, 14000 Kenitra, Morocco

Hydrogenated amorphous silicon (a-Si:H) thin films are prepared by radio frequency (R.F) sputtering from a monocrystalline silicon target, in an atmosphere composed of a mixture of argon and hydrogen gases. The substrate temperature was always 25°C . The argon pressure was kept at 10^{-2} mbar, and the partial pressure of hydrogen (P_H) was varied. Measurements of the optical transmission in the region 400 - 2400 nm, were carried out at room temperature in a varian DMS 100 double beam spectrophotometer. The structural properties have been investigated by X-Ray specular reflectivity.

The main results are:

- Taking the Urbach energy as an indicator of disorder in the material, we observe a linear dependence between Urbach energy (E_u) and optical gap (E_g) when the thickness or the partial pressure are varied.
- Correlation of the electron density of the layers with the variation in the optical constants.
- Stability of the films as regards the preparation parameters.

- E-I/P16** OPTICAL PROPERTIES OF LPCVD SILICON OXYNITRIDE, M. Modreanu, Institute of Microtechnology PO Box 38-160, Bucharest 72225, Romania; N. Tomozeiu, Faculty of Physics, University of Bucharest, PO Box 11 Mg, 5600 Bucharest, Romania; P. Cosmin, Cathalyst Semiconductor Inc., 1259 Borregas Avenue, Sunnyvale, CA 94089, USA and M. Gartner, Institute of Chemistry and Physics, Bucharest, Romania

Low pressure chemical vapour deposition (LPCVD) silicon oxynitride films of various composition (from pure SiO_2 to pure Si_3N_4) were deposited by changing the relative gas flow ratio $r = Q_\text{N}_2\text{O}/Q_\text{NH}_3$. The effects of oxygen on the physical properties of the films were studied using spectroellipsometry (using Bruggeman EMA approximation and Wemple Di Domenico model) and Fourier transform infrared spectroscopy. Refractive index measured by spectroellipsometry method are studied as a function of some deposition parameters: temperature of deposition, gases flux ratio. The high value of deposition temperature means low values in refractive index. More oxygen into films decreases the refractive index. The refractive index dispersion is studied by single-oscillator Wemple Di Domenico model. The optical bandedge varies monotonically from 4.5 eV for silicon nitride, to 9 eV for HTO LPCVD silicon dioxide and for the studied silicon oxynitride was found to be between 5.5 to 7 eV. Also some electrical properties are presented.

- E-I/P17** DEPOSITION OF MICROCRYSTALLINE SILICON FILMS BY MAGNETRON SPUTTERING, M. Tzolov, Y. Jeliazova, M. Sendova-Vassileva, D. Dimova-Malinovska, M. Kamenova, CLSENES-BAS, 72 Tzigradsko Chaussee, 1784 Sofia, Bulgaria

RF magnetron sputtering of c-Si target in atmosphere of argon and hydrogen have been used for deposition of $\mu\text{c-Si:H}$ films. The transition amorphous/crystalline film have been studied varying the hydrogen partial pressure. The crystallinity of the films have been determined by Raman scattering.

It have been observed that at fixed hydrogen and argon partial pressure the increase of the RF power leads to formation of amorphous films. The opposite behaviour were observed in the PECVD process [1]. It have been shown that the deposition rate is not limiting for the formation of the crystallite phase.

The films have been characterized by transmission in the far infrared and visible spectral region, PDS and reflection in the UV region. The hydrogen content estimated from the infrared spectra and the absorption in the vis/NIR spectral region reflect also the amorphous/crystalline film transition.

[1] B. Drevillon, I. Solomon, and M. Fang, Mat. Res. Soc. Symp. Proc. vol. 283 (1993) 455

- E-I/P18** HIGH QUALITY, RELAXED $\text{Si}_{1-x}\text{Ge}_x$ EPITAXIAL LAYERS FOR SOLAR CELL APPLICATION, K. Said, J. Poortmans, M. Caymax, R. Loo, Interuniversity Micro-Electronics Centre (IMEC), Kapeldreef 75, 3001 Leuven, Belgium; A. Daami, G. Bremond, INSA de Lyon (UMR 5511), 20 Av A. Einstein, 69621 Villeurbanne Cedex, France, O. Kruger, M. Kittler, Institute for Semiconductor Physics, Walter- Korsching Str. 2, 15230 Frankfurt (Oder), Germany

Epitaxially grown relaxed $\text{Si}_{1-x}\text{Ge}_x$ layers are of increasing importance for microelectronics and optoelectronic devices. Therefore, the necessity to minimize the density of threading dislocations in $\text{Si}_{1-x}\text{Ge}_x$ device layers is a critical issue. In this report $\text{Si}_{1-x}\text{Ge}_x$ layers with $x = 0.1$ which were grown on a Si (100) substrate by means of Reduced Pressure Chemical Vapour Deposition at 800°C , are characterized. The analysis carried out on the grown layers revealed a very high material quality indicated by the large diffusion length as deduced from the Electron Beam Induced Current (EBIC) measurements. Transmission Electron Microscopy (TEM) measurements showed that the dislocations do not extend inside the layer but are rather confined to the Si/SiGe interface, which resulted in a more dislocation free material.

On the level of application, solar cells were processed with these layers and characterized. The collected short circuit current and the measured Internal Quantum Efficiency (IQE) of the finished cells were higher than the corresponding values for Si cell, grown and processed under similar conditions.

- E-I/P19** SHAPE OF GRAIN SIZE DISTRIBUTIONS DURING THERMAL AND ION-INDUCED CRYSTAL GRAIN NUCLEATION IN a-Si, C. Spinella, S. Lombardo, CNR-IMETEM, Stradale Primasole 50, 95121 Catania, Italy, and F. Priolo INFM - Dipartimento di Fisica dell'Università di Catania, corso Italia 57, 95129 Catania, Italy

We report and discuss a large variety of processing conditions concerning the solid phase crystallization of amorphous silicon films, induced either by thermal annealing or by ion beam irradiation at high substrate temperatures. The morphological evolution of the amorphous towards the polycrystalline phase is investigated by transmission electron microscopy and it is interpreted in terms of a physical model containing few free parameters related to the thermodynamical properties of amorphous silicon and to the kinetical mechanisms of crystal grain growth. The transient regime is described in terms of the classical nucleation theory and by assuming that crystal growth at sizes below 1 nm follows a very slow kinetics, characteristic of a defect free crystalline cluster. Above this size, growth kinetics increases because it is dominated by a twin-defect assisted crystal growth mechanism. The present description fits quite well all of the morphological experimental data, spanning from grain size distributions to crystallized volume fractions and crystal grain densities as a function of the annealing time. A direct extension of this model explains also the data concerning the ion-assisted crystal grain nucleation. On the basis of this analysis, we propose a hybrid methodology, based both on pure thermal and ion-assisted processing, to engineer the polycrystalline structure and to achieve average grain sizes as large as 3 - 4 microns.

- E-I/P20** RAMAN ANALYSIS OF ANNEALING TIME INFLUENCE ON THE CRYSTALLIZATION OF LPCVD a-Si ON GLASS SUBSTRATES, J.-L. Alay and J.R. Morante, Departament d'Electrònica, Universitat de Barcelona, Avgda. Diagonal 645-647, 08028 Barcelona, Spain; T. Mohammed-Brahim, M. Sarret and O. Bonnaud, Groupe de Microelectronique et Visualisation, Campus de Beaulieu 11B, Université de Rennes 1, 35042 Rennes Cedex, France

The solid phase crystallization of LPCVD deposited a-Si thin films on glass substrates has been studied as a function of annealing time at 600°C . After various annealing times, the thin films, 1 micrometer thick, were analyzed by Raman scattering spectrometry, transmission electron microscopy (TEM) and x-ray diffraction (XRD). From the integration of the crystalline and amorphous peaks obtained in the Raman spectra measured from the back and front sides, one concludes that the crystallization nucleation sites firstly appear at the Si/glass interface. The ratio between the Raman peaks reveals the evolution of the crystallization towards the Si surface. TEM images indicate that the crystal growth proceeds columnarly from the interface to the surface and support the Raman data. Likewise, in situ Raman measurements have also been performed during the annealing process allowing to discuss the crystallization kinetics, from the amorphous to the crystallized phase.

- E-I/P21** IMPROVED CHARACTERIZATION OF POLYSILICON FILMS BY RESONANT RAMAN SCATTERING, V. Paillard and P. Puech, Lab. de Physique des Solides, Univ. P. Sabatier, 118 Route de Narbonne, 31062 Toulouse, France; B. Caussat and J.P. Couderc, Institut de Génie Chimique, 18 Chemin de la Loge, 31078 Toulouse, France; P. Temple-Boyer, LAAS, 7 Av. Colonel Roche, 31077 Toulouse, France; B. de Mauduit, CEMES, BP 4347, 31055 Toulouse, France

It is sometimes difficult to extract the information about crystallites from Raman spectra, particularly in Si films grown at low deposition temperature. The contribution of the a-Si phase, even in a small proportion, may impose a more or less empirical treatment of the spectra. We propose Raman scattering experiments in resonance with the Si direct gap at 3.4 eV, to enhance the crystal Raman signal to the detriment of the amorphous one. Thus, it is easy to obtain direct and accurate results about crystallites, since resonant Raman spectra can be fitted without any deconvolution operation. Some examples, including stress measurements, will be presented.

- E-I/P22** IN-SITU DIAGNOSTICS FOR PREPARATION OF LASER CRYSTALLIZED SILICON FILMS ON GLASS FOR SOLAR CELLS, G. Andrä, J. Bergmann, F. Falk, E. Ose, Institut für Physikalische Hochtechnologie, Helmholtzweg 4, 07743 Jena, Germany

Polycrystalline silicon thin film solar cells require a 5 to 50 μm thick layer of coarse grained silicon on a glass substrate. The preparation can be accomplished by a three step process. An a-Si:H layer 500 nm thick is deposited on glass by PECVD. By laser crystallisation it is converted into a seed layer consisting of grains several ten μm in size. Epitactic thickening is achieved by UV-laser irradiation during further a-Si deposition.

We report on the preparation processes and on the in-situ diagnostics which is necessary to set the experimental parameters, particularly the laser intensities, without removing the substrate from the deposition chamber. The correlation between the results of optical (reflection and transmission) and other (conductivity) measurements is discussed. It is investigated in which way the glass substrate influences the optical measurement.

- E-I/P23** **OBSERVATION OF (110) ORIENTED SILICON NANOCRYSTALS IN a-Si FILMS ON GLASS SUBSTRATES AFTER PULSE EXCIMER LASER TREATMENTS**, M.D. Efremov, V.A. Volodin, S.A. Kochubei, Institute of Semiconductor Physics SB RAS, pr. Lavrentjeva 13, Novosibirsk 630090, Russia; V.V. Bolotov, Institute of Sensor Microelectronics SB RAS, pr. Mira 55a, Omsk 644077, Russia
Anisotropy of Raman scattering intensity in different geometries versus angle between polarization vector of incident light and sample axis was experimentally discovered in system of Si nanocrystals in a-Si film. This effect can be interpreted as result of preferred (110) orientation of the nanocrystals formed by pulsed excimer laser treatments. Appearance of the (110) orientation in the case of ELA of a-Si/glass structures was observed, earlier using HREM. Moreover, it was observed that significant part of the nanocrystals were self-oriented in plane with angle disorientation less than 7° . Using the symmetry selection rules from (110) surface it was shown, that in the case of (110) oriented nanocrystals disoriented in planar directions there can not be anisotropy of Raman scattering intensity. It was calculated that the modulation of the intensities in different scattering geometries versus angle between polarization vector of incident light and sample axis depends on part of self-oriented nanocrystals. According to Raman data the part of self-oriented nanocrystals was 30% in sample a-Si:H (100 nm) on Corning 7059 after multipulses treatment by irradiation of excimer XeCl laser with wavelength 308 nm and pulse duration 5 ns. This result is in good correlation with HREM and TEM data concerning (110) textured poly-Si films which was manufactured using thermal annealing with preliminary excimer laser treatments. The electrical characteristics of these films were much better than its of films without laser treatments. It is supposed, that the effect of nanocrystal self-orientation can be result of influence of mechanical stresses appearing inside of amorphous films due to different densities of a-Si and crystalline Si. This work was supported by Russian Fund of Basic Research.
- E-I/P24** **POLY-Si TFT WITH EXCELLENT ELECTRONIC PROPERTIES USING METAL INDUCED LATERAL CRYSTALLIZATION**, H.S. Kwok, Z.H. Jin, G. Bhat, M. Wong, Hong Kong, University of Science and Technology, Department of Electrical and Electronic Engineering.
Metal induced lateral crystallization (MILC) is gaining popularity as a low temperature process for poly-Si TFT. We have performed a detailed study of the MILC process using nickel as the seeding metal. Using high resolution TEM and areal SEM scans, we were able to map the grain growth dynamics and the grain boundary structures during MILC. A nickel diffusion front could be observed. Nickel impurity both in front of and behind this front could be measured. Tiles of tiny grains of crystalline Si could also be observed. The mostly longitudinal grains have a profound effect on the characteristics of the TFT. We were able to achieve a Hall mobility of over $100\text{cm}^2/\text{Vs}$, an on-off ratio of over 10^7 , a low threshold of 2.2V, and a subthreshold slope of 0.66V/decade, at a low process temperature of 500C, WITHOUT hydrogen passivation.
- E-I/P25** **REAL TIME SPECTROSCOPIC REFLECTOMETER FOR END POINT DETECTION ON MULTICHAMBER DEPOSITION PROCESSES**, P. Boher, S. Noygues and J.L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France
Real time process control tools are more and more needed for the critical steps of IC technology. In the case of Thin film transistors (TFT) for Flat Panel Display (FPD) applications one of the critical steps is the deposition the Si_3N_4 /undoped a-Si/doped a-Si/ Si_3N_4 gate structures. For this purpose, BALZERS has developed a multichamber PECVD deposition system with limited deposition rates and high reproducibility and homogeneity (KAI concept). Even in these very well controlled process conditions a precise real time measurement of the layer has been developed for evaluation of day to day stability and reduction of the thickness dispersion in one batch. A xenon lamp is used to illuminate up to 20 optical fibers that enter to each reactor. A very simple optical setup allows to illuminate the center of the glass substrates at 87° of incidence from normal. After reflection, all the beams are focussed on 20 others optical fibers that enter the same high resolution prism spectrograph equipped with a multi-channel detector. The reactor is selected using shutters. The signal reading and pretreatment is made using a DSP board. Regressions including backface reflection effect are performed in real time (up to 6 reactors per second). Practical examples will be given in the case of Si_3N_4 and amorphous silicon depositions. Results will be compared to ex-situ measurements conventional spectroscopic ellipsometry.
- E-I/P26** **STATE CREATION INDUCED BY GATE BIAS STRESS IN UNHYDROGENATED POLYSILICON TFT's**, B. Tala-Ighil, A. Rahal, K. Mourgues*, A. Toutah, L. Pichon, T. Mohammed-Brahim**, F.Raoult*, O. Bonnaud*; Site Universitaire, LUSAC, BP78, 50130 Octeville, France; *GMV, UPRESA au CNRS 6076, Université Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France
The stability under high gate bias of the recent high performances n and p type unhydrogenated polysilicon TFT's realized in low temperature solid-phase crystallization technology, is studied. Undoped active layer and doped drain and source regions are amorphous deposited using low pressure chemical vapor deposition technique, and then in-situ solid-phase crystallized. Drain and source regions are in-situ doped using diborane for p-type and phosphine for n-type TFT's. Gate insulator is an atmospheric chemical vapor deposited SiO_2 layer. The maximum temperature used in this process is 600°C . The threshold shift ΔV_T is positive for n-type and negative for p-type TFT's. ΔV_T shows a power-law time $(t/t_0)^p$ dependence. The subthreshold slope increases and the transconductance decreases during these stresses. The density of the gap states, determined from the known field-effect analysis, increases during these stresses. Positive stress shows a slight increase of the DOS near the valence band VBT. A more important increase of this VBT and an increase of the DOS near the conduction band CBT are observed with negative stress. Moreover a high shoulder appears deeply in the lower half-gap. The disordered structure of polysilicon is involved to explain this state creation in unhydrogenated TFT's.
- E-I/P27** **NEW METHOD FOR DETERMINING THE EFFECTIVE CHANNEL LENGTH IN POLYSILICON THIN FILM TRANSISTORS**, F.V. Farmakis, J. Brini, G. Kamarinos, N. Mathieu, LPCS, ENSERG, 23 rue des Martyrs, BP 257, 38016 Grenoble Cedex 1, France and C.A. Dimitriadis, Department of Physics, University of Thessaloniki, 54006 Thessaloniki, Greece
It is well known that the accurate knowledge of the effective channel length in a polysilicon thin film transistor (TFT) is of great importance. The reduction ΔL of a channel length is due to lateral diffusion from the source and the drain into the gate region. The usual method for determining the reduction of the channel length consists in plotting the curve $1/I_d$ vs length mask in the linear region and by extrapolation ΔL is obtained. We show that this method is approximative and, especially in the case of n-type accumulation mode TFTs, it leads to an underestimation of the reduction channel length. We propose an alternative method by calculating the saturation current (I_{dsat}) and then by plotting $1/I_{dsat}$ vs channel mask length. We show that this method is more accurate, especially because the series resistance in the saturation region is no longer important. Our method gives interesting results, which are compatible with the functioning and the whole modelisation of the device, especially for n-channel accumulation mode TFTs. Its pertinence for extraction of the channel reduction ΔL of a TFT is found to be in full agreement with the physical explanation of the working of the device.
- E-I/P28** **TRANSPORT PROPERTIES OF $\mu\text{c-Si:H}$ ANALYZED BY MEANS OF NUMERICAL SIMULATION**, A. Fantoni, M. Vieira, R. Martins, Uninova, Quinta da Torre, 2825 Monte de Caparica, Portugal
Microcrystalline silicon is a two-phases material. Its composition can be interpreted as grains of crystalline silicon imbedded in an amorphous silicon tissue, with an high concentration of dangling bonds in the transition regions. The characteristics of each one of the two phases play an important role on the whole macroscopic properties. Nevertheless, $\mu\text{c-Si:H}$ has its own macroscopic characteristics, which are different from each one of the single phases characteristics. The crucial point in modelling a device based on microcrystalline silicon material is to determine the role played by the boundary regions between the crystalline grains and the amorphous matrix. If the distance between two adjacent grains is enough large this regions could be treated similarly to an heterojunction interface. The difference between the energy gaps and the intrinsic carrier concentration cause the presence of local electric field in this transition regions. In this paper are presented results, obtained by means of numerical simulations, about the grains boundary fields distribution and their influence on the internal electric configuration of an intrinsic $\mu\text{c-Si:H}$ thin film in thermodynamic equilibrium, under illumination and applied bias. The role of diffusion and drift mechanism on the carriers transport within the material will be outlined.

- E-I/P29** NITROGEN ADDED Al RARE-EARTH ALLOY FOR THIN FILM TRANSISTORS, T. Arai, H. Takatsuji, and H. Iiyori, IBM Yamato Laboratory, 1623-14 Shimo-tsuruma, Yamato-shi, Kanagawa 242, Japan
Bottom-gate thin-film transistors (TFTs) have been widely investigated for use in active-matrix liquid crystal displays (AMLCDs). In recent years, much effort has been devoted to developing low-resistivity gate bus lines, to meet the need for large, high-resolution LCDs. Aluminum (Al) is a remarkably good material for gate bus lines. However Al easily forms hillocks and whiskers during heating processes such as chemical vapor deposition (CVD) film formation, and also forms voids after heating processes. Hillocks causes defects as a result of short-circuits and current leakage between the gate and the upper electrodes, and voids disturbs electronic conduction. To increase stress migration resistance, many Al-based alloys and thermal protective structures have been reported.
In our study, nitrogen added Al-yttrium (Y) or Al-gadolinium (Gd) alloy were used as a gate metal. These films were reactive sputtered in an argon ambient containing nitrogen. These films have a strong resistance to hillock and void formation. Nitrogen effectively decreases the grain size, and smoothes the surface roughness of Al. The nanostructure and the surface morphology of the nitric Al-based alloys were studied by combined atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (TEM).
- E-I/P30** POLYPYRROLE-BASED CONDUCTING HOT MELT ADHESIVES FOR EMI SHIELDING APPLICATIONS, J.A. Pomposo and F.J. Rodriguez, CIDETEC, Center for the Electrochemical Research & Development, P^o Mikeletegi 61, 1^o, 20.009 San Sebastian, Spain
Intrinsically conducting hot melt adhesives have been developed, based on polypyrrole blends, for use in electronic and telecommunication applications requiring shielding against electromagnetic interference(s) (EMI).
These new products have been formulated to exhibit significant EMI shielding effectiveness (SE) while retaining the superior properties of conventional hot melt adhesives.
Potential use of such advanced materials in current and future electronic applications is anticipated.
- E-I/P31** SURFACE PASSIVATION OF Si BY RF MAGNETRON SPUTTERED SiN, M. Vetter, Institut für Physikalische Elektronik, Universität Stuttgart, Allmandring 19, 70569 Stuttgart, Germany
The electronic passivation of the silicon (Si) surface is important for the production of high efficiency solar cells. Very low surface recombination velocities S_{eff} are achievable with Si-rich silicon nitride (SiN) layers on p-Si [1]. In a previous work [2] we investigated how the interface state density (D_{it}) and the fixed charges (Q_f) depend on deposition temperature, hydrogen (H) content and annealing of sputtered SiN layers on p-Si. In this paper we show how S_{eff} depends on the deposition temperature, the H content and the Si content of sputtered SiN layers. The optical band gap is evaluated from spectral ellipsometry and decreases strongly for Si-rich SiN. Infrared spectra of sputtered and remote SiN show differences in the Si-H bands which is attributed to different deposition mechanisms. Using the microwave detected photoconductivity decay technique we determine S_{eff} of about 60 cm/s at a deposition temperature of about 200 °C for Si-rich layers sputtered on p-Si (0.35 Ωcm).
[1] T. Lauinger, J. Schmidt, A. G. Aberle, R. Hezel, Appl. Phys. Lett. 68,1232 (1996).
[2] M. Vetter, M. Jetter, Proc. 14th Europ. PVSEC, Vol. 2, p.2473 (H.S. Stephens & Associates, Bedford, 1997).
- E-I/P32** EFFECT OF ELECTRIC FIELD POLARITY CHANGE ON DEFECT CREATION IN MOS CAPACITORS, Dj. Ziane, A. El-Hdiy and G. Salace, LASSI / DTI (CNRS EP 120), Université de Reims, BP 1039, 51687 Reims cedex, France
Fowler-Nordheim tunneling electron injections under a high field in which polarities change during stress, are well known to be procedures for programming (write / erase) EEPROM (Electrically Erasable Programmable Read Only Memory) memories. The study of comparison of high field polarity effects on electrical behavior of MOS capacitors had revealed a dissymmetry in creation of oxide defects and of interface states [1]. The new approach suggested here consists of change the field polarity many times during stress in order to approach the write / erase cycles. In this work we used a MOS (Metal - Oxide - Silicon) structure 17.5 nm thickness. Stresses were made under 10 MV/cm. At each field polarity (V_g : the gate is negatively polarized, and V_g : it is positively polarized) we measured the density of injected current and fixed it to a same value of 0.16 C cm⁻². We deduced the density of both neutral oxide defects and interface states. Our observations are as follows: The density of interface states increases in the beginning (for a few number of cycles ≈ 5 ; one cycle means injection of 0.16 C cm⁻² under V_g followed by the same injection under V_g) to reach a relative "steady" state when cycles are repeated many times (30 times). The density of neutral oxide traps were deduced from [2]. The density of neutral traps localized near the oxide / silicon interface is higher than created near the metal / Oxide interface during the first cycles (≈ 5 cycles). This difference between the two neutral traps density decreases when the number of cycles increases.
[1] A. El-Hdiy et al., Thin Solid Films 296, 109 (1997)
[2] D.J. Dumin et al., J. Appl. Phys. 76, 319 (1994)

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

Poster Session II

17:00-19:00

- E-II/P1** **ROLE OF THE RESISTIVE LAYER ON THE PERFORMANCES OF a-Si:H THIN FILM POSITION SENSITIVE DETECTORS**, E. Fortunato, F. Soares and R. Martins, DCM/FCT-UNL and CEMOP-UNINOVA, Quinta da Torre, 2825 Monte de Caparica, Portugal
The 1D and 2D position sensitive detectors based on glass/TCO/a-Si:H(p.i.n)/metal structures present poor resolutions and linearity's close to the device edges that can be as high as 10%, compared with the device high resolution (better than 99%) and linearity (better than 99%) observed out of the device edges. This effect is attributed not only to non uniformity's of the device structure due to the variations on the thickness of the different constituents, but also to the electric field distortions. This problem can be solved by proper compensation of the collecting resistance and proper design of the shape of the electrodes. Apart from that, the metal contact should be used to improve the soldering of the external wires. The aim of this paper is to present the role of the collecting resistive layer and the design of its shape on the performances of 1D and 2D a-Si:H based position sensitive detectors. The main emphasis is put in solving the problem ascribed to the linearity distortion and loosen in resolution observed close to the device edges, besides the proper external wiring soldered to the metal electrodes. To do so, different collecting resistive layers were investigated, such as indium tin oxide, tin oxide and zinc oxide, for the collecting layer while a copper tin alloy was developed to improve the metal contact and the proper join of the contact to the external wiring. By proper selection of the most adequate sheet resistivity of the collecting layer and by using the proposed copper tin alloy to produce the metal electrodes and the join, an improvement on the device performances over the entire device range of more than 20% was achieved.
- E-II/P2** **GASEOUS POLLUTION DETECTION BY Pt DOPED SnO₂ THIN FILMS ON SILICON**, A.V. Tadeev, G. Delabouglise and M. Labeau, Laboratoire des Matériaux et du Génie Physique, Institut National Polytechnique de Grenoble, UMR 5628, BP 46, 38402 Saint Martin d'Hères, France
Polycrystalline Pt-doped SnO₂ films have been deposited onto silicon substrate by ultrasonically spray deposition. This technique provides a very fine and homogeneous dispersion of Pt aggregates (3-5 nm) inside the polycrystalline film. The metallic aggregates act as catalyst for a low temperature detection of pollutant gas as CO (25-100°C) by conductance change (sensitivity $S = (G - G_0)/G_0$ up to 60 at 100°C for 300 ppm CO in air). The influence of the synthesis temperature (400- 560°C), of the Pt additive concentration (1-12 wt. %), and of the carrier gas humidity on sensitivity has been studied. The realization of a gas sensor requires to provide a highly porous layer (thickness: ≈ 1 micron). The results of electrical responses under CO pollutant in air using dynamic regime and quasi-static regime are discussed. The narrow peak of gas sensitivity in the low temperature range (25- 100°C) is obtained for 9 wt. Pt % in the film. The selectivity for the CO detection has been examined in presence of water or alcohol as interfering gaseous species.
- E-II/P3** **FREQUENCY LIMITS OF MICROCRYSTALLINE P-I-N DETECTORS**, M. Vieira, F. Macarico, M. Fernandes, S. Koynov* and R. Schwarz**, ISEL, R. Conselheiro Emidio Navarro, 1900 Lisboa, Portugal; *CL-SENES, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria; **Phy. Dep., IST, Av. Rovisco Pais, 1000 Lisboa, Portugal
We have studied the frequency dependence of entirely microcrystalline p-i-n detectors in coplanar and transverse short-circuit current measurements. The samples with a thickness of 1.5µm were deposited by the cyclic CVD method on ITO-coated glass substrates. Two Cr dots on top of the n-layer, 5 mm apart, served as lateral contacts for coplanar measurements. Device I-V characteristics and spectral response curves were described previously.
In contrast to coplanar photocurrent response times of typically 100µs in undoped microcrystalline silicon, a much better time resolution of the p-i-n detector of about 5µs was measured. Furthermore, after the initial fast decay, a second much slower decay with a decay time of typically 480µs was seen.
From steady-state position-sensitive detector behavior one would expect the photocurrent to vanish in the central position of the incident beam. However, slow negative and positive current transients accompany the light pulse. In transverse mode, the time-dependence of the short-circuit current is dominated by the fast component alone.
A tentative explanation of these intriguing phenomena are given in terms of a combined action of fast recombination-controlled decays and slow space-charge capacitance effects.
- E-II/P4** **LASER-RECRYSTALLIZED POLYSILICON RESISTORS AND PIEZORESISTORS FOR MECHANICAL SENSORS**, A.A. Diuzhinin, E.N. Lavitska, I.I. Maryamova and Y.M. Khoverko, "Lviv Polytechnica" State University, Kotlarevsky Street 1, Lviv 290013, Ukraine
The influence of microzone laser recrystallization on the electrical and piezoresistive characterization of polysilicon layers on insulating substrates were studied theoretically and experimentally in order to reveal advisability of laser treatment in sensor technology. The dual action of laser recrystallization on poly-Si layers has been taken into account: enlarging of the average grain size and increasing of the electrically active doping impurity concentration. It is evident that both these changes are interrelated.
The studies make it possible to recommend for p-type poly-Si layers the concentration of electrically active boron in the range $1 \times 10^{18} - 5 \times 10^{19} \text{ cm}^{-3}$ for the laser recrystallization. Depending on parameters of the laser treatment the increase of longitudinal gauge factor from 1.5 to 2.3 times has been received.
Results of the studies were applied in the technology of the mechanical sensors with laser-recrystallized polysilicon piezoresistors.
- E-II/P5** **THERMAL STABILITY OF MODIFICATED SURFACES OF SILICON - BASED THIN DIELECTRIC FILMS FOR LARGE AREA ELECTRONICS**, V.S. Vasilenko, I.K. Doycho, Odessa State University, Physical Faculty, Non-Crystalline Electronic Systems Dept. (NIL-11), Odessa, Ukraine
Water adsorption on the surfaces of devices of large area electronics can decrease the electrophysical properties of these devices. To improve it the surfaces are usually modificadoed by special processing. For example, the silicon-based materials are annealed and immersed in hexamethyldisilazane (HMDS). In this paper we propose the new technique of evaluation of thermal stability of modificadoed surfaces, that based on measurements of the contact angles of water droplets at the investigated surface after annealing at various temperatures. The simple physical model allowed us to calculate the activation energy of HMDS radicals desorption.

- E-II/P6** SELF-ASSEMBLY OF SURFACE COMPOSITE TiO_2 /POLYMER ULTRATHIN FILMS, N. Kovtyukhova, Institute of Surface Chemistry, 31, Pr. Nauky, 252022 Kiev, Ukraine; P.J. Ollivier, The Pennsylvania State University, University Park, PA 16802, USA; S. Chizhik, A. Dubravin, Metal-Polymer Research Institute, 32A Kirov Str., 246652 Gomel, Belarus; E. Buzaneva, A. Gorchinskiy, National T. Shevchenko University, 64 Vladimirska Str., 252033 Kiev, Ukraine; A. Marchenko, Institute of Physics, 48 Pr. Nauky, 252022 Kiev, Ukraine
Self-assembly of metal oxide/polymer composite films with thickness control to nanometer precision is novel approach for the construction of advanced nanostructured materials for microelectronic applications. The self-assembly procedure consists of layer-by-layer deposition of metal oxide nanoparticles and organic macromolecules from aqueous sols. The deposited nanoblocks form layers alternating along the stacking axis and holding together by nonspecific bonding forces at the solid/solution interface. This work presents a detailed study of the preparation and characterisation (AFM, STM) of ultrathin TiO_2 /polymer films on Si and $\text{Al}_2\text{O}_3/\text{Al}$ substrates. The films have been prepared from stable TiO_2 hydrosols containing particles of 4-13 nm in diameter and aqueous solutions of polyethylenimine (P) and polyallylamine hydrochloride. It has been shown that the quality of the first TiO_2 layer and multilayer $(\text{TiO}_2/\text{P})_n\text{TiO}_2$ film is determined by the conditions of their deposition and the chemical composition of the substrate surface. The first TiO_2 layer deposited onto NH_3 -terminated Si surface is formed from separate particles agglomerates of 20-120 nm in diameter or islands of film consisting of the particles agglomerates of the same size. The first TiO_2 layer deposited onto $\text{Al}_2\text{O}_3/\text{Al}$ substrate completely covers the surface and consists of single particles and agglomerates of particles of 20-100 nm in diameter. The multilayer $(\text{TiO}_2/\text{P})_n\text{TiO}_2$ film deposited onto $\text{Al}_2\text{O}_3/\text{Al}$ substrate, has been shown, to be a uniform well-packed insulating layer.
- E-II/P7** HIGH QUALITY SPRAY DEPOSITED FLUORINE-DOPED TIN OXIDE FILMS FOR LARGE AREA ELECTRONICS, A. Malik, R. Nunes, E. Fortunato and R. Martins, FCT-UNL/CEMOP-UNINOVA, 2825 Monte de Caparica, Portugal
Among different large area preparation methods of highly transparent and conductive fluorine-doped tin oxide films (FTO) for different optoelectronic applications, spray pyrolysis stand out for its simplicity and low production cost. For the first time our work shows that this technique is also capable of producing microcrystalline FTO films with (200) preferred grains orientation and excellent electro-optical parameters (transparency in visible region above 80%, resistivity of $3 \times 10^{-4} \Omega \text{ cm}$, carriers mobility of $20 \text{ cm}^2/\text{V}\cdot\text{s}$ and concentration of 10^{21} cm^{-3}).
- E-II/P8** PERFORMANCES PRESENTED BY LARGE AREA ITO LAYERS PRODUCED BY RF MAGNETRON SPUTTERING, I. Baia, M. Quintela, L. Mendes and R. Martins, CEMOP-UNINOVA, Quinta da Torre, 2825 Monte de Caparica, Portugal
This paper presents the main characteristics exhibited by large area indium tin oxide (ITO) films (300 mm x 300 mm) produced by rf magnetron sputtering. The deposition process was carried out at room temperature, using an argon based pressure mixed with oxygen at different percentage concentrations. The films uniformity and homogeneity along the entire substrate area was highly improved by allowing a continuous movement of the substrate in front of the fixed cathode. The transparency and conductivity of the films was highly improved (more than 3 orders of magnitude) by first annealing the films at 470°C in air, followed by a reannealed stage under vacuum at 350°C , using a hydrogen atmosphere. In the following we present results concerning the role of the oxygen concentration and the deposition pressure on the films electro-optical characteristics, structure and morphology, after and before the annealing stages, as well as how the film's properties are distributed along the entire substrate area.
- E-II/P9** PERFORMANCES PRESENTED BY ZINC OXIDE THIN FILMS DEPOSITED BY SPRAY PYROLYSIS, P. Nunes, A. Malik, B. Fernandes, E. Fortunato and R. Martins, Materials Science Department of Faculty of Science and Technology of New University of Lisbon, 2825 Monte da Caparica, Portugal
Zinc oxide based thin films are of extreme importance in the optoelectronic field due to its excellent chemical and mechanical stability. In the present work, undoped and doped (aluminium and indium) zinc oxide thin films have been prepared by spray pyrolysis of a solution of zinc acetate and aluminium/indium chloride using an aluminium/indium -to- zinc ratio of 5 at %. The effect of doping and annealing atmosphere (argon or vacuum) on the performances of such films has been investigated concerning its role on the transport and structural properties of these films. The results indicate that the doping influence mainly the electrical and structural properties and less the optical properties. These data also show that doping with indium is more efficient than with aluminium ($\rho_{\text{ZnO:Al}}=142.2 \Omega \text{ cm}$ and $\rho_{\text{ZnO:In}}=1.55 \Omega \text{ cm}$). Annealing the as-deposited films lead to a substantial reduction in the resistivity and an increase on the degree of crystallinity film's, mainly under an argon atmosphere. The undoped film is the one in which the more significative change in films performances were achieved. The films doped with indium presents a resistivity of $0.013 \Omega \text{ cm}$ and a visible transmission of the order of 80%, meaning the possibility to use them for several optoelectronic device applications such as solar cells and optical sensors. For applications as gas sensors the film with the better properties is ZnO without post-deposition heat treatment because this one have the highest resistivity ($580 \Omega \text{ cm}$) and the sensitivity of the sensors increase with the resistivity.
- E-II/P10** POLARIZATION PHOTOSENSITIVITY OF ITO/Si SOLAR CELLS, V.Yu. Rud', State Technical University, 29 Polytekhnicheskaya st., 195251 St. Petersburg, Russia; Yu. V. Rud', A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 26 Polytekhnicheskaya st., 194021 St. Petersburg, Russia and V.M. Botnaryuk, State University, Kishinev, Moldava
Transparent conducting oxides are widely used as a wide band gap window, which simultaneously acts as an antireflection coating with a low surface layer resistance. In the present article we report in the first time the results of an experimental study of the photoelectric processes in ITO/Si devices in linearly polarized radiation (LPR). The solar cells were produced using a n-type (111) silicon plate. The ITO films were deposited on the n-Si plates at temperatures from 400 to 500°C . The efficiency of the solar cells obtained was equal to 10-12 %. Polarization photosensitivity and an increase in the quantum efficiency of the photoconversion as a results of a decrease in the reflection losses were found. The induced photopleochroism coefficient P_1 increases with the angle of incidence Θ as $P_1 \sim \Theta^2$. The polarization photosensitivity of ITO/Si devices was studied as a function of the photon energy between the energy gaps of the two contiguous materials. Oscillations of the P_1 were also observed. The antireflection effect is maximum as $P_1 \rightarrow 0$. The maximum azimuthal current photosensitivity at $\Theta=70^\circ$ reaches $80 \text{ mA/W}\cdot\text{deg}$. Therefore, ITO/Si devices can be used as a broad-band polarimetric sensors.
- E-II/P11** RAMAN SCATTERING IN HIGHLY CONDUCTIVE AND TRANSPARENT IN THE VISIBLE RANGE ZnO FILMS, N. Tzenov, M. Tzolov, D. Dimova-Malinovska, M. Kalitzova, T. Telbizova, CLSENES-BAS, 72 Tzigradsko Chaussee, 1784 Sofia, Bulgaria; C. Pizzuto, G. Vitali, University 'La Sapienza', Via A. Scarpa 14, 00161 Rome, Italy; I. Ivanov, Linköping University, IFM / FYSIKHUSSET, 581 83 Linköping, Sweden
Highly conductive and transparent in the visible range ZnO films doped with Al have been deposited by RF magnetron sputtering. The RHEED measurements have shown strong orientation of the crystallites with the c-axes perpendicular to the substrate and a random rotation around it. The mean crystallite size have been estimated by X-ray measurements to be 30 nm. The AFM images from the surface have given a mean size of the grains on the surface of about 35 nm. In this paper we report upon the Raman spectra of these samples measured at different temperatures and with different wavelength of the laser light. Surprisingly, the Raman spectra of the films have been completely different from those of the target material, i.e. of the polycrystalline ZnO . They are dominated by the LO vibrations at about 576 cm^{-1} and a band at 276 cm^{-1} . The latter have been assigned to a disorder-induced vibration. The high intensity of the LO bands have been explained by the enhancement of the scattering efficiency in electric field. In the case of ZnO such a field is formed on the grain boundaries. Additional bands appear at 466 cm^{-1} and 516 cm^{-1} which seem to originate from surface phonon modes. The Raman spectra excited with UV radiation reveal that amorphous phase is also present in the films.

- E-II/P12** **TiN THIN FILMS DEPOSITION BY RF REACTIVE SPUTTERING: APPLICATION TO OPTOELECTRONIC DEVICES**, M. Balucani, V. Bondarenko, L. Franchina, G. Lamedica and A. Ferrari, INFN Unit E6, University 'La Sapienza', Rome, Italy; and G. Dinescu, B. Mitu, C. Stanciu, V. Sandu*, M. Dinescu, IFA, NILPRD, PO Box MG-16, 76 900 Bucharest, Romania *NIMP, PO Box MG-26, 76 900 Bucharest, Romania
Silicon based optoelectronic devices is a very widespread research and application field due to the explosion produced by the discovering of photoanodelectro-luminescence of porous silicon, photoluminescence of other Sinanostructures and microcrystalline silicon applications. Large area structures together with appropriate high conductive materials are mandatory requirements for the applications. Titanium nitride as high conductive, corrosion and erosion resistant film is proposed to be used as top electrode for porous(π) Si based devices as well as for bottom electrode and diffusion barrier for microcrystalline Si based devices. The TiN thin film have been deposited in a RF reactive sputtering system with planar electrodes at a pressure of 0.1-0.5 torr in a mixture of Ar/N₂ containing a few percent of nitrogen. A DC voltage supply has been additionally used to enhance the sputtering and deposition rates. The experimental conditions for obtaining transparent TiN layers were identified. Techniques as X-ray diffraction, Fourier Transform Infrared Spectroscopy, Electron Microscopy, Spectroellipsometry, have been used to characterize the deposited structures. Plasma spectroscopy studies were performed to correlate the properties of films with the presence of different excited species in the rf discharge. Optical and electrical measurements of the TiN / π -Si structure, confirm the good properties of the TiN as a transparent conductive electrode contact, which, can be deposited, using this methode, on large area.
- E-II/P13** **SYNTHESIS OF OXIDE-BASED CONDUCTIVE LUMINESCENT THIN FILMS FOR FIELD-EMISSION DISPLAYS**, V. Bondar, M. Vasylyv, M. Grytsiv, Y. Dubov, S. Popovich, L. Akselrout, V. Davydov, V. Vasylytsiv, Lviv State University, Department of Physics, 50 Dragomanov Str., 290005 Lviv, Ukraine
The luminescent thin films based on Zn₂SiO₄:Ti with blue emission, ZnGa₂O₄:Mn, ZnO:Zn - with green, and Y₂O₃:Eu, Gd₂O₃:Eu, Zn Gd₂O₃:Eu, ZnGa₂O₄:Cr - with red color of emission were synthesized using RF-magnetron sputtering technique with subsequent thermal annealing. After annealing at T>1000 °C the films were polycrystalline with grains size about 70 nm and showed bright luminescence. Using modified RF-magnetron sputtering technique nanocrystalline films with grain sizes about 20 nm were obtained without any post-annealing. Cathodoluminescent efficiency of thin film phosphors is about 2-4%. Annealing in hydrogen reducing atmosphere leads to increasing of thin films conductivity for ZnGa₂O₄:Mn up to 10² times, for Zn₂SiO₄:Mn - 10² - 10³ times, for Ga₂O₃ - 10³ times, and for ZnGd₂O₃:Eu - 10³ times. Increasing of conductivity is caused by shallow donor levels created by oxygen vacancies. The red and green luminescent structures ZnGa₂O₄:Cr/ ZnO:Zn on quartz substrates were developed and investigated. The effect of inter-epitaxy of [111]-oriented ZnGa₂O₄ and [001]-oriented ZnO films was found. It results in improving of crystal structure and luminescence efficiency of thin film phosphors.
- E-II/P14** **LASER PULSE CRYSTALLIZATION AND ANNEALING OF THIN FILMS PHOSPHOR MATERIALS**, B. Kotlyarchuk, D. Popovych, V. Savchuk, Pidstryhach Institute for Applied Problems of Mechanics and Mathematics National Academy of Sciences of Ukraine, 3 b Naukova Street, 290601 Lviv, Ukraine
The results of the theoretical and experimental investigations of processes of pulse laser reactive crystallization and annealing beforehand deposited of the amorphous films of phosphor materials are presented in the paper. The amorphous thin (ZnO, Y₂O₃, ZnGa₂O₄) films were deposited on cold substrates from melted quartz by laser ablation ($\lambda=1.06\mu\text{m}$, $\tau=10$ -15 ns) of stoichiometric target. We used the method, that makes it possible to carry out the laser crystallization ($\lambda=1.06\mu\text{m}$, $\tau=10$ -100 ns) of amorphous thin films on substrate into the quasi-closed reaction space at oxygen pressure ($P_{\text{O}_2}=10^{-2}$ -10⁻³ Pa). On the base of selected heat-physical model and experimental investigation temperature fields curve distributions we obtained that in ZnO-SiO₂ system after laser radiation due with different energy both at direct effect and on the back side of quartz substrate, transparent for laser radiation. It was established that in the latter case laser radiation energy is in basic absorbed by amorphous film and temperature gradient in it are practically absent. That enables to carry out single-phase structural homogeneous crystallization. Laser annealing of crystalline thin films allows not only to increase crystalline structure perfectness but also electrically activate doped states and to liquidate precipitates. Thus obtained results of properties phosphorous materials and technological peculiarities of their obtaining may be the evidence of great potencies of using laser crystallization here.
- E-II/P15** **XPS CHARACTERIZATION OF TUNGSTEN BASED CONTACT LAYERS ON 4H-SiC**, A. Kakanakova-Georgieva, Ts. Marinova, Institute of General and Inorganic Chemistry, 1113 Sofia, Bulgaria, L. Kassamakova, R. Kakanakov, Institute of Applied Physics, 4000 Plovdiv, Bulgaria, O. Noblanc, C. Arnodo, S. Cassette, C. Brylinski, Thomson-CSF/LCR, 91404 Orsay Cedex, France
4H-SiC is a promising semiconductor for high-temperature device applications where stable metal contacts are of a great need. In this report the interfaces WN(W)/4H-SiC have been examined by X-ray photoelectron spectroscopy (XPS) after annealing. The 800°C annealed WN/SiC sample is characterized by steep and chemically inert interface. The 1200°C annealed WN(W)/SiC samples are characterized by significant carbon diffusion into the contact layer, tungsten carbide and tungsten silicide formation at the interface. The 800°C annealed WN/SiC contact is found to be of a Schottky type with a barrier height of 0.91 eV. The Schottky barrier height and the ideality factor show no significant changes during 100 hours storage at 500°C under nitrogen as well as during operation at increasing temperature up to 350°C in air.
- E-II/P16** **ACTIVE MATRIX DISPLAY WITH PILLARED NANOSTRUCTURES OF Al AND Ta ANODIC OXIDES**, E.A. Outkina, A.I. Vorobyova, Belorussian State University of Informatics and Radioelectronics, P.Brovky str.6, 220027 Minsk, Belarus
Active driving matrix fabricated by electrochemical processing of Al-Ta thin film compositions has been investigated. The matrix includes row and column buses integrated with driving pixels at the intersections. Each pixel consists of the MDM element with non-linear current-voltage characteristic, and pillared nanostructure formed on the top MDM electrode by anodizing of Al-Ta film composition and covered with deposited thin metal film. Pillars are 300(600 nm in height, 30(120 nm in diameter with density (2,5-5,0) (1010 cm⁻². Effective pixel size is 180 micrometers. Each pillared pixel is surrounded by the row gate electrode, and the column is connected with the bottom MDM electrode. The matrix is developed for active addressing of large-scale plasma and electroluminescent display panels.

SYMPOSIUM E

- E-II/P17** DEEP SUBMICRON 3D SURFACE METROLOGY USING UV/BLEU SCANNING INTERFEROMETRY, P. C. Montgomery, Laboratoire PHASE, CNRS, 23 rue du Loess, 67037 Strasbourg, France; D. Montaner, LEPSI, 23 rue du Loess, 67037 Strasbourg, France; C. Kazmierski and S. Bouchoule, France Telecom, CNET Paris B, Laboratoire de Bagneux, 92220 Bagneux, France
Feature sizes of 0.25 μm can presently be achieved at production line level in microelectronics fabrication by optical microlithography using UV light sources and computer controlled illumination. While optical metrology provides some interesting solutions for rapid, quantitative analysis of surface structures, with nanometric or better axial resolution, there is a need for these techniques to make use of shorter wavelength illumination as well in order to improve the lateral resolution. Scanning optical interferometry is a fairly recent technique that has been used successfully for checking critical dimensions and calibrating processes. Using broadband, short coherence light in an interference microscope, a thin probe plane is scanned over the surface relief to provide measurement of shape. A high measurement speed is achieved through the parallel data acquisition provided by a CCD camera.
While white light is often used to limit the coherence temporally, we have recently shown that by using a high numerical aperture objective the coherence can also be limited spatially. Shorter wavelength light and even coherent sources can therefore be used to improve the lateral resolution. In this paper we present some of the latest results in the technique and discuss its possible application to the characterisation of 300 mm wafers.
- E-II/P18** NEW VANADIUM DOPANT PRECURSOR (VCl_4) FOR GaAs GROWN BY METALORGANIC VAPOUR PHASE EPITAXY, A. Rebey, A. Bchetnia, B. El Jani, LPM-Faculté des Sciences, 5000 Monastir, Tunisie; C. Ben Jeddou, Faculté des Sciences Bizerte, Tunisie; P. Gibart, CHREA-CNRS, 06560 Valbonne, France
We study the growth of vanadium doped GaAs by metalorganic vapour phase epitaxy (MOVPE) using vanadium tetrachloride (VCl_4) as a novel dopant source. The influence of growth temperature and flow rate of VCl_4 on the vanadium concentration in the GaAs epitaxial layers were examined. The incorporation of vanadium in GaAs were investigated by correlation between ambient Hall effect, secondary ion mass spectroscopy (SIMS) measurements and growth conditions. In order to measure the effectiveness of V in compensating the Si donors the GaAs was co-doped with silicon (Si) from silane (SiH_4) source.
- E-II/P19** AN ADVANCED MOCVD PROCESS BASED ON A COMBINED SYNTHESIS/TRANSPORT OF METAL CHELATES, O.V. Polyakov, A.M. Badalian, V.I. Belyi, Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, 3 Lavrentiev Ave., Novosibirsk, 630090, Russia
A novel technique for film deposition from metalorganics has been developed as an extension of the traditional MOCVD towards a simultaneous combination of synthesis/transport of volatile metal chelates. The chelate formation occurs while the organic ligand vapour passing through the column packed with grains of non-volatile precursor due to heterogeneous reaction on the grain surface with the product sublimation. The film grows at the substrate placed downstream near the reaction zone.
Owing to this technique we succeeded in simultaneous synthesis/deposition of chelated Y, Ba, Cu from the solid cuprate precursor resulted in the uniform glassy film formation. The film studies using UV- and IR-spectroscopy, XPS, Ellipsometry, Stripping VA- metry and the Differential Dissolution assay with ICP detection have induced us to suspect that metal transport may occur through heterometallic polynuclear complexes. Moreover, the metal stoichiometric ratio in the film could be readily controlled by variation of the solid precursor stoichiometry.
- E-II/P20** NEW ORGANIC FILM PHOTOSEMICONDUCTOR SYSTEMS FOR ELECTRONIC TECHNIQS, L. Kostenko, D. Mysyk, A. Popov, Y. Skrypnik, Institute of Physical Organic & Coal Chemistry of National Academy of Sciences of Ukraine, 70 R.Luxemburg str., Donetsk 340114, Ukraine
On the basis of using the effect of structural factors of n-donors and n-acceptors, and also different additives, dependences of photoconductors properties in spectrum region of 500-800 nm are obtained. Photoconductor systems-layers on the base of organic complexes with a charge transfer containing oligomeric matrixes with varying donor links (carbazol) and n-acceptors of fluorene series and also additives improving transfer of hole charge have been elaborated on the basis of these studies. Materials underwent tests in the series of compositions for different registration systems on hard and flexible substrates in interferometry and other informational systems.
Principal informational parameters:
1. Maximum potential of charging, V/mkm, 180 - for films on the glass substrate; 180 - for films on the lavesan support;
2. Dark droop of potential in % for 20 sek. 5-10; 5-10;
3. Electrophotographic sensitivity, m^2/Dj , for 633 nm.-10-12; 10-12;
4. Holographic sensitivity $\text{Sn}=1\%$, m^2/Dj , on 633 nm. 300; 150;
5. Maximum permissible value of diffractive effectiveness is 20; 15;
6. Level of parasite memory is 0.02; 0.02;
7. Cyclicity (recording-erasing) is 2000-15000; 1000-1500.
- E-II/P21** PECULIARITIES OF PHOTOINDUCED OPTICAL ANISOTROPY IN POLYMER FILMS, V.N. Ermakov, A.S. Trofimov, Bogolyubou Institute for Theoretical Physics, NASU, 252143 Kiev, Ukraine, L.I. Shansky, A.G. Tereshchenko, Institute of Physics, NASU, 252650 Kiev, Ukraine
The investigation of photoinduced optical anisotropy in polymer films containing azo-dye molecules has been carried out. The films were irradiated by polarized laser light with frequency near the maximum of absorption band of trans-isomer form of azo-dye molecule. Laser irradiation induced in films dichroism and double refraction of light. The value of double refraction increased with time of irradiation and after long time one came to the saturation level. However, in case of intensive laser light it was found that at the beginning of irradiation the magnitude of double refraction can be more than the saturation level. When irradiation went on with time the double refraction diminished to the stationary level. Thus, there was shown the effect of oversaturation of double refraction at beginning time of irradiation.
The theory explaining this phenomenon is proposed. According to one the effect is stipulated by retardation of induction of local film deformation near azo-dye molecules. The local deformation induces the opposite transition of azo-dye molecules from cis-form to trans-form. The nonlinear equations describing kinetics of induction and relaxation of double refraction were obtained. The theory also explains other experimental results.
- E-II/P22** FIELD-ASSISTED FEMTOSECOND PUMP-PROBE MEASUREMENTS IN CONJUGATED SYSTEMS, C. Zenz, G. Lanzani, University of Sassari, Via Vienna 2, 07100 Sassari, Italy; G. Cerullo, S. De Silvestri, Politecnico di Milano, P.za Leonardo da Vinci 32, 20133 Milan, Italy; W. Graupner, F. Meghdadi, G. Leising, Inst. f. Festkoerperphysik, Petersgasse 16, 8010 Graz, Austria
We present field-assisted femtosecond pump-probe experiments in light emitting diodes of ladder-type poly(para-phenylene)(LPPP) and parahexaphenylene (PHP). By modulation of the applied field we monitor directly the field-induced population of photo-generated species. The observed kinetics elucidate the mechanism of the charge carrier generation mechanisms in conjugated systems. The direct observation of the charge carrier generation in LPPP and its kinetics indicates a direct dissociation of singlet excitons into polarons. In PHP we observe a field-induced quenching of the singlet exciton leading to the formation of triplet excitons via an intermediate charged species.

- E-II/P23** SOL-GEL PROCESSING OF PT AND PZT FERROELECTRIC THIN FILMS, R.K. Hovsepyan, A.R. Pogosyan, E.S. Vartanyan, Institute for Physical Research Armenian National Academy of Sciences, Ashtarak-2, 378410, Armenia and A.L. Manukyan, S.G. Grigoryan, R.S. Vardanyan, Armenian Scientific Research Institute of Applied Chemistry - ARIAC, Yerevan, Armenia
The investigations of the crystallization's dynamics of the PT (PbTiO₃) and PZT (PbZrTiO₃) thin films on the substrates of silicon, sapphire and metallic nickel by the means of sol-gel method have been carried out. These studies allow to obtain the homogeneous ferroelectric thin films with spontaneous polarization both perpendicular and parallel to substrate's surface. The control of quality has been carried out by the electronic microscope and roentgen-phase method.
The investigations of the absorption spectrums of PT, PZT and PT, doped by Cu impurity (0-5%), in UV and visible region have been carried out and the model of fundamental absorption has been suggested on the base of these studies.
The possibility of creation of tunable dielectric filters is shown and the first studies on creation of the heterostructures (high temperature superconductor- ferroelectric thin film- HTSC) have been made.
- E-II/P24** PHENOMENA OF THE PHOTOPOLARIZATION ON BARRIER ORGANIC STRUCTURES, B. Roman, Non-Linear Sensors Laboratory, Drohobych State Pedagogical Institute, I. Franko str. 24,293720, Drohobych, Lviv Region, Ukraine
The experimental Me (Metal), SnO₂-PbPc-Me and SnO₂-Pn-Me results of investigation of the photoelectric processes in the SnO₂-VOPc-barrier structures are presented. If such samples which is turned off from the source of external tension to light by the right-angled impulse of light then at the beginning moment of the time the considerable short-circled current (I_s) can be observed. During the process of lighting (I_s) is diminishing monotonously to the stationary value which practically doesn't depend on the duration of lighting. When the lighting are stopped we can observe the current of depolarization which has opposite tension. Obtained voltage-current characteristics have showed that photopolarization can be observed only on sandwich structures (SS) with barrier top electrodes. The best material for such electrodes there are aluminum. Application of Ni also gave as barrier top electrodes for VOPc and pentacene. Copper and gold - for PbPc. Carried out calculation of characteristic times of the photopolarization and depolarization show that these times are different. There are very interesting information in date obtained from darkness current kinetic measurement. The conclusion was made that all these effects was created by injection of charge from electrodes.
- E-II/P25** INSULATING LAYERS OF POLYCRYSTALLINE GaAsS COMPOUNDS GROWN BY REACTIVE PLASMA SPUTTERING, O. Pesty, P. Canet, F. Lalande, J.L. Seguin, H. Cacharno, Laboratoire EPCM, Case A62, Faculté des Sciences de Saint Jérôme, 13397 Marseille Cedex 20, France
GaAsS ternary compounds are obtained from reactive radio-frequency cathodic sputtering of a monocrystalline gallium arsenide target in an argon and sulfurous hydrogen plasma. Thin films deposited on temperature controlled molybdenum substrates enable us to obtain a sandwich structure : Au/GaAsS/Mo.
Electrical (current-voltage) characterizations show a change, with sulfur concentration, in the compound behavior, from a highly doped semiconductor to a heavily insulating material.
Maximum serial resistivity ($4 \cdot 10^{13} \Omega \cdot \text{cm}$) is attained with a sulfur concentration of 50% (Arsenic concentration being nearly 0%) and a typical Space-Charge-Limited (SCL) conduction is obtained.
We determine dielectric permittivity from capacitive measurements.
This material presents insulating properties (varying with sulfur concentration) equivalent to those of SiO₂ compounds. Moreover epitaxial layers can be grown on GaAs substrate, which will lead to applications in GaAs technologies as an insulator or an interface (with a varying lattice parameter).
- E-II/P26** EPITAXIAL LAYERS $\text{Zn}_x\text{Cd}_{1-x}\text{Hg}_{1-x-y}\text{Te}$ ($0 < x < 0.18$, $0 < y < 0.12$) AND HETEROINTERFACES $\text{ZnCdHgTe-Hg}_{1-x}\text{Cd}_x\text{Te}$ ($0 < x < 0.80$): OPTICAL & ELECTRICAL CHARACTERISTICS, G. Khlvap, M. Andrukiv, Pedagogical Institute, 24 Franko str., Drohobych 2937207, Ukraine
The quaternary solid solution ZnCdHgTe had been created as an alternative material for well-known narrow gap semiconductor HgCdTe in order to stabilize weak Hg-Te bonds and to improve structural and optical characteristics. The investigations of this new material properties were carried out on the best samples of ZnCdHgTe layers grown by modified Te-rich technology [1]. Large area (up to 80 mm²) samples (the epilayer thickness was in range of 7-10 μm) were examined morphologically in situ and revealed the block surface structure with typical element size of 0.1 μm . The optical investigation had been shown the photosensitivity of obtained epilayers in wave length range 8-14 μm in temperature interval 77-180 K. The analogical studies provided for heterointerfaces ZnCdHgTe-HgCdTe were shown the replacement of photosensitivity peaks in range 3-7 μm at $T=200-230$ K. The variation in both epilayer and substrate composition creates additional possibilities for current transport and optical processes controllability.
[1]. N.L. Bazhenov, A.M. Andrukiv, V.I. Ivanov-Omskii Infrared Physics 34 357 (1993).
- E-II/P27** DEPENDENCE OF SEEBECK COEFFICIENT ON THICKNESS OF PYRITE THIN FILMS, J.R. Ares, I.J. Ferrer, J.F. Fernandez and C. Sanchez, Dpto. Fisica de Materiales, Facultad de Ciencias, Universidad Autonoma de Madrid, Cantoblanco, 28024 Madrid, Spain
Pyrite thin films is a promising material for larger area photovoltaic applications. To this aim, it is relevant to have a detailed knowledge of the transport properties of the films. The dependence of the Seebeck coefficient (S) on thickness (from 0.1 μm to 1 μm) of pyrite thin films has been investigated and is now reported. Films have been prepared by thermal evaporation of Fe, which are afterward, sulphurated under a sulphur pressure of 600 Torr and different temperatures ($423\text{K} \leq T \leq 723\text{K}$). Values of S change with T , from that corresponding to Fe ($S \approx 8 \mu\text{V/K}$) to $S \approx 70-80 \mu\text{V/K}$, presented by the films sulphurated at the higher temperatures ($\approx 723\text{K}$). In all the cases S changes following a sigmoidal curve but the exact evolution from one value to the other depends on the pyrite film thickness. It has been observed a decrease of S with the increase of the pyrite thin film thickness at low sulphuration temperatures ($T \approx 523\text{K}$). At higher sulphuration temperatures ($T \geq 573\text{K}$) S remains essentially constant and no significant influence of thickness on S has been observed. The evolution of the S with film thickness is discussed by considering the formation and crystallization of the films. (Supported by DGICYT, PB96-0084).
- E-II/P28** DETERMINATION OF THE CRYSTALLOGRAPHIC ORIENTATION IN PbTiO_3 EPITAXIAL FILMS USING OPTICAL SECOND HARMONIC GENERATION, E.D. Mishina, N.E. Sherstyuk, E.Ph. Pevtsov, A.S. Sigov, and O.A. Aktsipetrov, Moscow Institute of Radioengineering, Electronics and Automation, Moscow 117454, Russia, A.M. Grishin, Royal Institute of Technology, Stockholm, Sweden
 PbTiO_3 epitaxial films have potential application in microelectronics as nonlinear dielectrics that can be used for non-volatile memory elements and arrays. Reduction of the size of the electronic devices requires a reliable tool for their diagnostics. We suggest here a techniques for nonlinear optical diagnostics of thin epitaxial films, that is based on the second harmonic generation (SHG) and can be applied "in situ" during preparation. The SHG techniques being extremely sensitive to any changes of the crystal symmetry allows one to study the film local crystallographic orientation with the spatial resolution (several microns for in-plane direction and several atomic layers in thickness) and accuracy that exceed these characteristics for conventional techniques. We report here the results of the SHG diagnostics of thin epitaxial PbTiO_3 films on YBaCuO/LaAlO_3 substrate with the use of a femtosecond Ti-Sapphire laser.

E-MRS'98 SPRING MEETING



SYMPOSIUM F

Techniques and Challenges for 300 mm Silicon: Processing, Characterization, Modelling and Equipment

Symposium Organizers

- H. RICHTER** Institute for Semiconductor Physics, Frankfurt (Oder), Germany
- P. WAGNER** Wacker Siltronic AG, Burghausen, Germany
- G. RITTER** SEMITOOL Inc, Kalispell, USA

The assistance provided by

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(Austria)

is acknowledged with gratitude.

SYMPOSIUM F

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - 300 mm Fabs

F-I.1 09:30-10:00 - Invited - 300 MM CONVERSION - CHALLENGE AND BREAKTHROUGH FOR FUTURE SEMICONDUCTOR MANUFACTURING, P. Kücher, D. Tull, K. Roithner, M. Hiatt, Semiconductor 3000 GmbH Co. KG, Germany

F-I.2 10:00-10:30 AUTOMATISATION AND FAB CONCEPTS FOR 300 MM WAFER MANUFACTURING, A. Honold, Jenoptik, INFAB, Jena, Germany and H. Binder, Meissner + Wurst, Stuttgart, Germany

10:30-11:00 **BREAK**

SESSION II - 300 mm Rapid Thermal Processing

Joint with Symposium I

F-II.1 11:00-11:30 - Invited - MODELLING AND OFF-LINE OPTIMIZATION OF 300MM RAPID THERMAL PROCESSING SYSTEM, **A. Tillmann**, STEAG AST Elektronik GmbH, Daimlerstrasse 10, 89160 Dornstadt, Germany

The modelling of a new 300mm Rapid Thermal Processing (RTP) system is described. Conventional raytracing technique is used to determine lamp intensity distributions on both 200 and 300mm wafers. Simulation results are verified using the "difference method" (difference between two process parameter distributions such as oxide thickness, where the absolute power of one single lamp is varied) and using wafers instrumented with multiple thermocouples.

Wafer rotation is incorporated in the model and its influence on the temperature distribution will be discussed.

Off-Line optimization of the temperature distribution is done using model-based control. Experimental results of implant annealing, Rapid Thermal Oxidation (RTO) and silicidation processes on both 200 and 300mm are shown and critical parameters influencing the temperature uniformity are discussed.

11:30-14:00 **LUNCH**

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III - Crystal Growth and Epitaxy

- F-III.1** 14:00-14:30 - Invited - **LARGE DIAMETER SILICON TECHNOLOGY AND EPITAXY, H. Yamagishi, M. Kuramoto, Y. Shiraishi, M. Machida, K. Takano, N. Takase, T. Iida, J. Matubara, H. Minami, M. Imai and K. Takada, Super Silicon Crystal Research Institute Corp., 555-1 Nakanoya, Annaka, Gunma 379-0125, Japan**
 Japan Key Technology Center and seven Japanese silicon wafer manufacturing companies established Super Silicon Crystal Research Institute Corporation (SSI) in 1996. SSI will establish the key technologies to serve as the production platform of silicon wafers with a super large-diameter of 400 mm by January in 2001. SSI has three laboratories, crystal growth, wafer shaping and epitaxial growth. We introduce the targets of each laboratory and discuss key technologies. We mainly discuss our concept for large diameter silicon crystal growth such as reduction of electric power consumption in CZ furnace, a cusp magnetic field and anti-vapor explosion system. A crystal suspending system should be developed since the weight of CZ grown Si single crystal becomes heavier than 400 kg. Flatness, cleanness and particles with a diameter of less than 0.4 micrometer on 400 mm Si wafers are important issues. 400 mm epitaxial Si wafer grown at relatively low temperature may be dominant in Giga-bit era.
- F-III.2** 14:30-15:00 **TECHNOLOGY AND EQUIPMENT FOR THE GROWTH OF SILICON CRYSTALS WITH DIAMETERS OF 300 MM AND MORE, B. Altekruiger, Leybolds Systems GmbH, Germany**
- F-III.3** 15:00-15:30 - Invited - **CHALLENGES FOR ECONOMICAL GROWTH OF HIGH QUALITY 300 MM Cz Si CRYSTALS, E. Tomzig, W. von Ammon, E. Dornberger, U. Lambert, W. Zulehner, Wacker Siltronic AG, 84479 Burghausen, Postfach 1140, Germany**
 The changeover from 200mm to 300mm is required by semiconductor industry due to necessity for larger chip sizes and demand for decreasing costs. However, cost for 300mm growth are likely to rise owing to larger puller, enlargement of hot zone, expensive silica crucibles and longer growth process times caused by lower growth rates and longer cooling rates. Simultaneously the conditions are more complex and disadvantageous to get equal or the required higher qualities in comparison to smaller wafer diameters (i. e. position of OSF-ring, oxygen precipitation).
 This paper gives an overview about the challenges for 300 mm growth and approaches to provide appropriate solutions (i. e. application of magnetic systems, optimization of growth conditions by integration of numerical simulation).
- F-III.4** 15:30-16:00 **300 MM EPITAXY CHALLENGES AND OPPORTUNITIES FROM A WAFER MANUFACTURER'S POINT OF VIEW, P.O. Hansson, M. Fuerfanger, Wacker Siltronic AG, PO Box 1140, 84479 Burghausen, Germany and Y. Makarov, Friedrich-Alexander-Universität, Cauerstrasse 4, 91038 Erlangen, Germany**
 The transition to 300mm wafers involves technological challenges both relating to the increase in wafer diameter and to the shift in design rule to 0.18µm (0.13µm). Furthermore, the commercial challenge of increased wafer and equipment cost puts new restrictions on yield management and process monitoring.
 This paper discusses technological issues like thermal stress, epitaxial layer uniformity, and epitaxy crystal defect generation in the light of the industry's new requirements.
 Experimental data on 300mm Si slip line generation, crystal defect generation, layer thickness and resistivity uniformities, and gate oxide integrity are presented.
 The influence of Si substrate quality, in particular surface- and crystal defect concentration, on the epitaxial layer quality is discussed.
 Results of modeling a trichlorosilane (TCS) epitaxy process for optimizing the uniformity of deposition on a large area substrate are presented. The model includes coupled simulation of global heat transfer and gas mixture flow, taking into account the gas phase chemical decomposition of TCS and the growth kinetics on the Si wafer surface.

16:00-16:30

BREAK

SYMPOSIUM F

SESSION IV - Bulk Material Properties

- F-IV.1** 16:30-17:00 - Invited - **STUDY OF OXYGEN TRANSPORT IN CZOCHRALSKI GROWTH OF SILICON**, G. Müller, A. Mühe, Y. Makarov, Universität Erlangen, Institut für Werkstoffwissenschaften, Erlangen, Germany; E. Dornberger, E. Tornzig, W.v. Ammon, Wacker Siltronic AG, Burghausen, Germany
- F-IV.2** 17:00-17:30 **VACANCY DISTRIBUTION MEASUREMENTS IN Cz Si CRYSTALS GROWN BY DIFFERENT PULLING RATE**, Y. Takano and K. Kakumoto, Department of Materials and Technology, Science University of Tokyo, 2641 Yamazaki, Noda-shi, Chiba, 278-0114, Japan
Polyhedral void type defects in as-grown Si crystals are known to be very harmful in silicon devices, because they degrade the gate oxide integrity of MOS devices. Generation of the polyhedral void defects is considered to be closely related with vacancies in the Si crystals, however, there is few experimental results of it, because it is difficult to measure the vacancy precisely. In this report, we try to estimate the vacancy density in Si crystals grown with different pulling rate by measuring the deep levels which are induced by N₂-vacancy complexes.
It is found that the vacancy concentration is very low inside the OSF-ring and a little low in the ring region. Two kinds of the vacancy density profiles are observed in the wafers without the OSF-ring which are prepared from Si crystals grown by fast (1.4 mm/min) and slow (0.4 mm/min) pulling rate: one is gradual and the other is abrupt variation. We interpret the profiles by considering density distribution of the void defects in the wafer: the gradual variation is caused by the macroscopic defect density distribution and the abrupt variation is induced by the microscopic one accompanied with the growth striation.
- F-IV.3** 17:30-18:00 **UNIFORM PRECIPITATION OF OXYGEN IN LARGE DIAMETER WAFERS**, G. Kissinger, J. Vanhellemont*, U. Lambert*, D. Gräf, and H. Richter, Institute for Semiconductor Physics, Walter-Korsing-Str. 2, 15230 Frankfurt (Oder), Germany; *Wacker Siltronic AG, P.O. Box 1140, 84479 Burghausen, Germany
In the present stage of development, 300 mm crystals often contain a transition from vacancy-rich to interstitial-rich which is not located at the perimeter of the crystal. Due to this radially varying concentration of self-interstitials and vacancies, the radial size distribution of grown-in oxide precipitate nuclei is also inhomogeneous in these wafers. Especially in the region of the transition from vacancy-rich to interstitial-rich, the oxygen precipitation behavior can therefore change abruptly with the radial position. It will be shown that, although the radial variation of the point defect type and distribution strongly influences the size of the oxide precipitate nuclei, a dedicated thermal treatment leads to a total density of precipitates which is constant over the whole wafer. In order to achieve a radially uniform internal gettering efficiency in 300 mm wafers, a slow temperature ramp induced growth of all grown-in oxide precipitate nuclei is the appropriate procedure to overcome problems resulting from the inhomogeneous size distribution of grown-in nuclei. This approach is based on the observation that in contrast with the nuclei size distribution, the nuclei density distribution is homogeneous over the wafer independent of the dominant intrinsic point defect.
- F-IV.4** 18:00-18:30 **EFFECT OF THE STRUCTURAL STATE OF THE MELT ON THE PROPERTIES OF SILICON CRYSTALS**, A.Ya. Gubenko, Moscow Institute of Electronics and Mathematics, ul. Kuusinen 25, Moscow, 125252, Russia
In molten silicon and silicon crystals grown from the melt containing impurities in specific concentration ranges (SCR), phase changes occur by which silicon, using the trial-and-error method, seeks, through persistent large-scale fluctuations, for a new state (phase). These fluctuations form within the SCR a sequence of equilibrium microstates differing in the forces of interatomic interaction and, consequently, in the whole body of structural and electro-physical properties of both the melts and crystals that form from these melts. For this reason, the properties of the melts (crystals) change within SCR in an oscillating manner. The properties of the melts with a disordered structure near the solidification point are the same as those of the melts outside the SCR or as those that are overheated by about 200 K. Silicon crystals grown from the melt with the disordered structure have unique properties.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION V- 300 mm Challenges and Opportunities

- | | | | |
|--------------|-------------|-------------|--|
| F-V.1 | 14:00-14:30 | | CHARACTERIZATION OF 300MM SILICON WAFERS, <u>S. Shih</u> , C. Au, Z. Yang, H. Huff and R. Goodall |
| F-V.2 | 14:30-15:00 | - Invited - | 300 MM WAFERS - A TECHNICAL AND AN ECONOMICAL CHALLENGE, H. Dietrich, W. Bergholz, S. Dubbert and C. Drabe, Siemens AG, München, Germany |
| | 15:00-15:30 | | 300 MM PROCESSES AND PROCESS CHARACTERIZATION CHALLENGES, W. Schönleber |

SESSION VI - Panel Discussion

15:30-17:00 **THE 300 MM TECHNOLOGY - GLOBAL OPPORTUNITY FOR INDUSTRY AND CHALLENGES FOR RESEARCH**

- The silicon materials roadmap
- Technology driven demand
- Coordination and partnerships among Silicon wafer, IC equipment suppliers and IC manufacturers
- Silicon wafer requirements
- Metrology, international standards

Tentative Participants:

Siemens AG, Jenoptik AG, Wacker Siltronic, SSI, Semitool, FhG, Semiconductor 300, BMBF, IHP

Thursday June 18, 1998
Jeudi 18 juin 1998

Morning
Matin

SESSION VII - 300 mm Wafer Surfaces

F-VII.1 8:30-9:00

DISCRIMINATION OF PARTICLES AND DEFECTS ON SILICON WAFERS, F. Passek, H. Piontek, A. Luger and P. Wagner, Wacker Siltronic AG, P.O. Box 1140, 88479 Burghausen, Germany

The classification of imperfections and contamination on surfaces of silicon wafers becomes increasingly important for determining origins of defects and their elimination. However, conventional defect characterization performed with microscopes or other time consuming tools does not meet the requirement of a fast and effective quality and process control.

Investigations on the fast Surface Scanning Inspection Systems (SSIS) based on detecting scattered laser light reveal that a discrimination of particles against other defects is possible by a more detailed analysis of their scattering behavior.

The scattered light intensity as a function of its emission angle depends on the nature of the scattering object. In the present investigation the capability for defect discrimination of the commercial SSIS, Tencor SP1 which detects light scattered into two different solid angles was studied. The data recorded with this system allows a discrimination between particles and other defects with high probability. However, the degree of discrimination is neither unique nor complete. The particle separation depends on the substrate and on the defect size.

F-VII.2 9:00-9:30

ALKALINE CLEANING OF SILICON WAFERS: ADDITIVES FOR THE PREVENTION OF METAL CONTAMINATION, A. Martin, B.O. Kolbesen, J.W. Goethe-University, Frankfurt/Main, Germany; W. Hub, Siemens AG, Semiconductor Group, Muenchen, Germany; P. Mertens, M. Baeyers, H. Schmidt, IMEC, Leuven, Belgium

F-VII.3 9:30-10:00

CONTAMINATION SURFACE ANALYSIS OF THE LARGE SIZE Si WAFERS BY TXRF METHOD USING OF WIDE DIVERGENT PRIMARY X-RAY BEAM, V.K. Egorov, A.P. Zuev, Lab. Nucl. Phys. IPMT RAS, Institute prospect 19, 142432, Chernogolovka, Moscow dist., Russia

The most vulnerable areas of the standart Total Reflection X-Ray Fluorence Spectrometry TXRF [1] are the procedure complexity of the surface target orientation about X-Ray primary direction and a trifle of the surface diagnostic zone. Acuteness of this factors is enhanced as increasing as a testing space. However such problems may be disregarded if the TXRF measurements will be produced by using the slitless X-Ray collimator [2] with wide divergent angle of the primary beam in plane of the quartz blocks formed the slitless collimator.

The peculiarity of the collimator design are discussed. The variation of the exciting X-Ray intensity over all testing target surface is evaluated. The preliminary experimental data included are shown the high efficiency of the surface contamination analysis at the testing of the large area wafers. There is received serious attmption to problems of the structure's reflexes repression in TXRF spectra and the background level reduction stipulated by primary beam scattering on oxygen and nitrogen atoms. TXRF procedure with wide angle slitless X-Ray collimator and standart tube (2 kW) with Mo anode allows to achieve in a large size Si wafer study the detection limits for Fe group elements up to $1 \cdot 10^{10}$ at/cm².

[1] Handbook of X-Ray Spectrometry, Methods and Techniques, eds. R.E. Van Grieken, A.A. Markowicz, Marcel Dekker Inc., New York, 1993, p-p. 453-490.

[2] V.N. Leikin, T.A. Mingazin, V.I. Zelenov, Pribory i Teknika Experimenta, #6, 1984, p-p. 33-36, in Russian.

10:00-10:30

BREAK

SESSION VIII - High Temperature Processes

F-VIII.1 10:30-11:00 - Invited -

MECHANICAL STRENGTH OF 300 MM DIAMETER Si WAFERS AT HIGH TEMPERATURES: MODELING AND SIMULATIONS, A. Fischer, H. Richter, Institute for Semiconductor Physics, Walter-Korsing-Str. 2, 15230 Frankfurt (Oder), Germany; R. Knott, P. Krottenthaler, R. Wahlich, Wacker Siltronic AG, POB 1140, 84479 Burghausen, Germany

Under gravitational and thermal constraints of IC process technology, 300 mm diameter Si wafers can partly relax via slip dislocation generation and propagation, degrading the electrical characteristic of the leading edge device.

We present a force balance model to describe the strain relaxation in large wafer diameter, which includes heat transfer effects and the criterion for yielding under a plane stress state. The material attributes, e.g., oxygen and its state of aggregation, are taken into account. While the plastic deformation of Si wafers caused by thermal stresses at high temperatures can be controlled by process design, the control of plastic deformation due to gravitational forces may be accomplished by equipment design.

This system approach allows calculation of wafer mechanics and ramp rate profiles for an arbitrary high-temperature process. The quantitative theory proposed here provides guidance for computer simulation to configure stable slip-free wafer process flow under mechanical and thermal loads. Applications include high speed simulations for use in "what if?" experiments or initial simulations of large scale experimental sequences.

SYMPOSIUM F

- F-VIII.2** 11:00-11:30 - Invited - **EXPERIMENTAL VERIFICATION OF DIFFERENT SLIP GENERATION MODELS FOR 300 MM WAFERS PROCESSED IN A FAST RAMP VERTICAL FURNACE, G. Ritter, P. McHugh, G. Wilson, L. Funk, and P. Zaumseil*, Semitool, Inc., 655 West Res. Drive, Kalispell, MT 59901, USA, *Institute for Semiconductor Physics, W. Korsing Str. 2, Frankfurt (Oder), Germany**
 This paper presents the results of wafer slip tests conducted using Semitool's 300 mm Express Furnace. Two different wafer support configurations are investigated in processes at temperatures from 900 C to 1150 C. X-ray diffraction topography is used to search for the presence of dislocations in wafers processed. The experimental data is evaluated against the predictions of the wafer stress analysis code MacWafer/ PCWafer [1]. This code enables the application and evaluation of different slip generation models [2,3]. Tests at temperatures below 950 C employ a conventional tower design, in which wafers are supported at three edge positions separated by 90 degrees. In this work, wafer pitch values of 22mm, 11mm, and 5.5mm were studied corresponding to the use of 30, 60, and 121 slots, respectively. Thermal process tests at temperatures above 950 C are performed using a test tower design in which wafers are supported at three interior points located at a radial position equal 70% of wafer radius. These points have an angular separation of 120 degrees. The wafer pitch value was 11mm. Instances of wafer slip are observed only at the contact points with the wafer support. The occurrence of wafer slip is best described by the model attributable to reference [3] assuming an oxygen precipitation level of about 4ppm.
 [1] R. Nilson and S. Griffiths, MacWafer Computer Software, Sandia National Laboratories, Livermore, CA 94551-0969.
 [2] M. Schrems, et al., in Semiconductor Silicon'94, H.R. Huff, W. Bergholz, and K. Sumino, Eds., 1050-1063, The Electrochemical Society, Inc., N.J.
 [3] B. Leroy and C. Plougonven, J. Electrochemical Society 127, N4, 961-970 (1980).
- F-VIII.3** 11:30-12:00 **CHALLENGES AND CURRENT STATUS IN 300 MM RTP PROCESSING, M. Glück, U. Kreiser, M. Merkwitz, S. Frigge, P. Schmid, and W. Lerch**
- F-VIII.4** 12:00-12:30 **SOLID PLANAR SOURCES OF BORON AND PHOSPHORUS FOR HIGHLY UNIFORM DOPING OF LARGE DIAMETER SILICON PLATES, V.O. Voronin, Y.M. Bogdanovski, L.Z. Hasko, V.M. Myshchyshin, Electrophysical Dpt., State University "Lviv Polytechnic", 12 St.Bandera Street, 290646 Lviv, Ukraine**
 Solid planar diffusion sources (PDS) of boron and phosphorus are carried out for highly uniform doping of large diameter 200-300 mm silicon plates. Our new technology of PDS manufacturing for diffusion doping of large diameter silicon plates is described in this paper. It is based on the both sides drawing of the silicon wafer by diffusion materials.
 Materials on the base of aluminium boron silicon are used for boron doping (850 - 1150 °C) and polycrystalline $\text{Al}(\text{PO}_3)_3$ (925 - 1100°C), $\text{LaP}_5\text{O}_{14}$ (800 - 925°C)-for phosphorus doping. The disorder surface resistivity over the silicon plates does not exceed $\pm 2\%$. Each PDS is reusable during 100 hours under maximum temperatures, providing reproducibility and uniformity of doping results due to high contents of active materials. Undesirable impurities amounts do not exceed 10-5% in the doping process. Besides PDS thermal stability and resistance are comparable with silicon plates analogous parameters and preliminary PDS preparation is not necessary.
- 12:30-14:00 **LUNCH**

Thursday June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-Midi

SESSION IX - Characterization and Metrology

- F-IX.1** 14:00-14:30 - Invited - NOVEL PROCESS CONTROL STRATEGIES FOR 300 MM SEMICONDUCTOR PRODUCTION, L. Pfitzner, C. Schneider, Fraunhofer Institut für Integrierte Schaltungen, Erlangen, Germany
- F-IX.2** 14:30-15:00 SPECULAR AND DIFFUSE X-RAY SCATTERING FROM SILICON SURFACES: A USEFUL TOOL FOR QUALITY CONTROL, R. Stömmmer, H. Göbel, Siemens AG, Corporate Technology, Otto-Hahn-Ring 6, 81739 Munich, Germany and U. Pietsch, University of Potsdam, Institute of Physics, Am Neuen Palais 10, 14469 Potsdam, Germany
With the down-scaling of integrated circuits, surface and interface roughness must be controlled to achieve high yielding integrated circuits.
For roughness determination of high quality surfaces and thickness control of ultra-thin layers, X-ray scattering proves to be an innovative tool. Applying a parabolic X-ray mirror as beam condensor, we obtain a high incident flux of parallel X-rays for the scattering experiment.
We demonstrate that specular and diffuse X-ray scattering from a silicon surface with a 2nm oxide allows the precise determination of roughness, density and density grading, oxide thickness, lateral correlation length and surface fractal dimension. X-ray scattering is non-destructive. It should be considered as an analytical support at "front end processes" of integrated circuit fabrication.
- F-IX.3** 15:00-15:30 NOVEL METHOD, FOR 300 MM SILICON WAFER CHARACTERIZATION IN VLSI TECHNOLOGY, V.M. Popov, V.A. Denysyuk, A.V.Klimenko, Research Inst for Microdevices Phys & Techn Res Cert Center, 3, Severo-Syretskaia, 254136 Kiev, Ukraine
Electrically active defects (EAD) at insulator-semiconductor (IS) interface are one of the most important surface irregularities which play an essential role in performance and reliability of IC fabricated on large diameter wafers. Novel method for determination of local electrophysical parameters of EAD responsible for the values of bulk generation life-time of minority carriers in MIS structures has been developed. The new technique enables to study internal properties of submicron size EAD using traditional test structures. The method is based on analysis of pulse-modulated dynamic unsteady-state current-voltage characteristics of MIS structures. The essence of the method is that special conditions in MIS structures are created owing to which local EAD properties can be strictly distinguished from integral properties of the whole structures. Method for EAD analysis in Si-SiO₂ structures with very thin oxides (30-100°A) has been created. Method is based on application of nematic liquid crystals (NLC). Under definite conditions scanning NLC probe reveals rapidly different kinds of EAD on oxidized Si surface. Method and equipment for non-destructive determination of EAD responsible for recombination of minority carriers in Si wafers has been developed. Discrete scanning of Si wafers by focused laser beam (5microns) generates photoelectronic signals which form corresponding EAD images on computer display.
- 15:30-16:00 **BREAK**
- F-IX.4** 16:00-16:30 SOPRA SE300: A NEW TOOL FOR HIGH ACCURACY CHARACTERIZATION OF MULTILAYER STRUCTURES, P. Boher, M. Bucchia, J.P. Rey and J.L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France
In order to characterize 300mm wafers at different stages of the IC manufacturing, a new tool based on spectroscopic ellipsometry has been recently developed at SOPRA. This new instrument called SE-300 has some important new features compared to the other ellipsometers of SOPRA or of the competition. First the optical setup allows to obtained very small measurement spots down to 35x45µm in polychromatic light to be able to work from deep UV 190nm to near infrared; second the combined monochromator/spectrometer is directly setup on the analyser arm and allows both multichannel and scanning measurements on the same spot. Scanning measurement made with a real double monochromator including prism and grating allows very accurate measurement that can be used to extract optical indices and solve complex multilayer structures. Multichannel measurement are made through a prism/grating spectrometer with quasi linear dispersion in wavelength. The detector includes an intensifier before a multichannel photodiode array connect to the computer through a DSP board. Intensifier is usefull to increase the signal /noise ratio especially in the deep UV region. All the system is designed to be used on line in production directly on the real wafers. All the elements (robotics, prealigner, XYZ mapping, pattern recognition) are fully compatible with the new generation of 300mm wafers. Practical results obtained in real environment (I300I acceptance tests and MEDEA project) will be presented.

SYMPOSIUM F

F-IX.5 16:30-17:00

ACCURATE INFRARED ABSORPTION MEASUREMENT OF THE INTERSTITIAL OXYGEN CONCENTRATION IN P+ SILICON WAFERS, O. De Gryse, P. Clauws, University of Gent, Krijgslaan 281, 9000 Gent, Belgium; L. Rossou, J. Van Landuyt, RUCA-EMAT, Groenenborgerlaan 171, 2020 Antwerpen, Belgium, and J. Vanhellemont, Wacker Siltronic AG, P.O. Box 1140, 84479 Burghausen, Germany
Heavily p-doped 300 mm Cz-Si wafers will be extensively used as substrates for epitaxial layers, in order to avoid problems arising from crystal defects in the near surface region of Cz-Si. As the wafers of the 300 mm generation will be both sided polished, external gettering using the backside of the wafer becomes increasingly difficult thus increasing the importance of internal gettering techniques. Although boron is an efficient getterer for different transition metals, it is expected that the additional gettering by SiO_x precipitates will be needed to increase yield. To study the behaviour of oxygen it is necessary to be able to determine the interstitial oxygen (O_i) concentration. For moderately doped Si-wafers Fourier Transform Infrared (FT-IR) spectroscopy is the standard technique. However, low resistivity material is not transparent in the mid-IR region because of the free carrier absorption which dominates the infrared light absorption. Other techniques, like gas fusion analysis (GFA), have therefore been developed and are extensively used to determine the total oxygen content, leaving the oxygen configuration - precipitated or interstitial - uncertain. In this contribution a novel method is outlined to measure the interstitial oxygen concentration in heavily boron-doped silicon by measuring at low temperature the height of an oxygen related absorption peak. The results are compared with the oxygen concentration obtained from GFA data and from FT-IR data of similar samples irradiated with a high fluence of 2 MeV electrons.

F-IX.6 17:00-17:30

FEMTOSECOND DIAGNOSTICS OF *Si(001)*-BASED MOS STRUCTURES BY PHOTOINDUCED AND DC-ELECTRIC FIELD INDUCED SECOND HARMONIC GENERATION, M. Anderson, P. Wilson, and M.C. Downer, Physics Department, The University of Texas at Austin, Austin TX 78712, USA; M.L. Lyubimova, E.D. Mishina, and O.A. Aktsipetrov, Department of Physics, Moscow State University, Moscow 119899, Russia

Photoinduced effects in DC-electric field induced second harmonic generation (EFISH) are studied experimentally and theoretically in $\text{Si-SiO}_2\text{-Cr}$ MOS structures at the subpicosecond time scale that gives the means of MOS structure diagnostics. The size of the silicon wafer up to 300 mm does not restrict the potentialities of the techniques suggested.

Experimental EFISH studies are performed using pump-probe configuration and photomodulation technique, for which two beams of the splitted output of a tunable femtosecond Ti-Sapphire laser are used as a pump and probe radiation. The pump beam generates electron-hole pairs in conduction band of subsurface Si layers, whose injection changed the space charge region parameters of the MOS structure. The probe beam generates the second harmonic radiation from the silicon subsurface regions with photomodified parameters. Photomodulation efficiency depends on applied bias and photon energy and allows one to measure the local (with the spatial resolution about several microns) parameters of MOS structure: silicon doping concentration, interface trap concentration and the surface recombination constant.

END OF SYMPOSIUM F

Notes

E-MRS'98 SPRING MEETING



SYMPOSIUM G

Surface Processing: Laser, Lamp, Plasma

Symposium Organizers

- | | |
|--------------------|---|
| J. PERRIERE | Groupe de Physique des Solides, Universités Paris VII et Paris VI, Paris, France |
| M. STUKE | Max-Planck-Institut für Biophysikalische Chemie, Göttingen, Germany |
| I.W. BOYD | Electronic & Electrical Engineering, University College London, London, UK |
| U. BIERMANN | Philips Reserach Laboratories, Eindhoven, The Netherlands |

SYMPOSIUM G

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I

Chairperson: E. Fogarassy, CNRS, Laboratoire PHASE, Strasbourg, France

- G-I.1** 8:30-9:00 - Invited - **UV LASER INDUCED PLASMA AND RELATED APPLICATIONS, C. Boulmer-Leborgne, J. Hermann, A.L. Thomann, E. Sicard and C. Vivien, GREMI, Université d'Orléans, BP 6759, 45067 Orléans cedex 2, France**
 There is a growing interest in the use of pulsed UV lasers for applications such as thin film deposition, material analysis or surface property modification. The laser induced plasma plays an important role in each of these applications and many authors report on its creation and expansion mechanisms. Nevertheless it seems to be difficult to obtain a complete and precise knowledge of all the involved phenomena from vapour ionisation to plasma expansion. During the laser pulse time, both processes implying photons, i.e. multiphoton ionisation and inverse Bremsstrahlung effect, have to be considered to explain the electron density growth. Then the electron energy and density gain and loss balance includes the collisional processes and diffusion phenomena. The knowledge of the plasma parameters like electron density and temperature is necessary to characterize the physical and chemical abilities of this energetic medium. During its ionisation step, the plasma can be described by a local thermodynamic equilibrium that vanishes in the following recombination phase in which chemical reactions can occur in reactive ambient gas. The ionisation degree in the plasma and its species kinetics depend on the laser material interaction parameters and on the nature and pressure of the ambient. Experimental investigations based on spectroscopic studies and modelling give such informations. The interest of the plasma study for the process control will be examined in relation with associated applications.
- G-I.2** 9:00-9:15 **SIZE, ANISOTROPY AND DISTRIBUTION OF Cu NANOCRYSTALS PREPARED BY PULSED LASER DEPOSITION, R. Serna, C.N. Afonso, Instituto de Optica, C.S.I.C., 28006 Madrid, Spain; A. Naudon, D. Babonneau, LMP, UMR 6630 du CNRS, UFR Sciences, bat SP2MI, Bd 3 Téléport 2, France; A.K. Petford-Long, Department of Materials, Univ. of Oxford, Oxford OX1 3PH, UK**
 Metal nanocrystals embedded in dielectric matrixes exhibit special optical and electrical properties, which depend on the nanocrystals size, shape and distribution. The fabrication of such materials in thin film configuration for use in integrated optoelectronic devices is still a major challenge. Pulsed laser deposition is a suitable technique with potential to develop these nanocomposite films for waveguide applications. Films consisting of Cu nanocrystals in an Al₂O₃ matrix are deposited by independent ablation of Cu and Al₂O₃ targets, either in vacuum or in an Ar environment. The average dimensions and distribution of the Cu nanocrystals have been determined both by grazing-incidence small-angle X-ray scattering performed using a synchrotron source, and high resolution transmission electron microscopy. The Cu nanocrystals are randomly distributed in the film plane with average diameters ranging from 2 to 4 nm and average separation from 6 to 8 nm depending on the number of pulses applied to the Cu target during deposition. When the number of pulses increases both the average separation and the nanocrystals anisotropy increases, the nanocrystals becoming ablate ellipsoids. The results obtained for nanocrystals grown in vacuum and gas pressure are compared and discussed in terms of the nucleation and growth mechanism.
- G-I.3** 9:15-9:30 **WORK FUNCTION VARIATION DURING UV LASER-INDUCED OXIDE REMOVAL, Cs. Beleznaï*, D. Vouagner and J.P. Girardeau-Montaut, Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard - Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France; *also at the Department of Experimental Physics, Jozsef Attila University, 6720 Szeged, Dom t. 9., Hungary**
 Photocurrent measurements yielded new data, which were used to determine the surface work function of a native oxide-covered tungsten photocathode. The photoemission was generated by a continuous UV source. The surface work function has been measured at various stages of a pulsed UV laser-induced oxide removal in order to characterize the process. Since the measured surface work function can be correlated with the surface coverage, along with the measurements of charge of laser-induced photoelectrons and surface reflectivity a description of the laser-oxide interaction is presented. Based on the effective medium approximation a coverage-dependent reflectivity response is calculated and compared to the measured reflectivity data. A fully computer-controlled experimental setup is demonstrated, achieving photoelectric measurements at the spot of laser illumination. This apparatus enables us to follow the work function temporal dependence during laser illumination, thus giving a detailed description for the surface coverage dynamics.

SYMPOSIUM G

G-I.4 9:30-9:45

PULSED LASER DEPOSITION OF $\text{Li}_x\text{Mn}_2\text{O}_4$ AND LiCoO_2 THIN FILMS, M. Morcrette, A. Laurent, P. Barboux*, J.A. Chaos, Groupe de Physique des Solides, Universités Paris VII et Paris VI, Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France; * Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cedex, France

LiMn_2O_4 and LiCoO_2 are possible materials as a positive electrode in secondary Li ion cells. In this work, we have studied the growth of thin films by laser ablation of LiMn_2O_4 and LiCoO_2 targets for electrochemical applications. Films have been deposited onto Si (100), MgO (100), Al_2O_3 (001) and ZrO_2 (001) at different T (300 to 700°C) under oxygen pressure (10^{-6} to 1 mbar).

The amount of Li has been determined by Nuclear Reaction Analysis. It increases when T decreases and when pressure increases. The stoichiometric composition LiMn_2O_4 has been obtained under 0.2 mbar and 500°C. X-Ray diffraction analysis indicates the formation of the spinel phase when films are grown under high oxygen pressure. On Si (100) films are polycrystalline with a 8.23 Å lattice parameter. On ZrO_2 and alumina substrate films they are textured with a (111) orientation. This corresponds to the dense oxygen planes of the spinel structure parallel to the substrate. On MgO substrate, films are very well textured with their c axis normal to the substrate. In this last case, a large amount of Mg has been detected in the films by RBS except for films grown under vacuum for which films a Mn_2O_4 type phase is evidenced. Then we can assume that MgO participate to the growth of the spinel phase. RBS in channeling geometry show a high crystalline quality for these films with a χ_{min} close to 7%. A similar behaviour has been checked for LiCoO_2 thin films but no Mg has been detected.

G-I.5 9:45-10:00

SPATIO-ENERGETICAL CHARACTERISTICS OF LASER PLASMA IN CROSS-BEAM PLD. A. Tseley, A. Gorbunov, W. Pompe, Institut für Werkstoffwissenschaft, TU Dresden, 01062 Dresden, Germany

Cross-beam pulsed laser deposition (CBPLD) is established as a PLD technique that allows an effective refinement of the laser ablation plasma from the molten phase droplets. However, the efficiency of the consumptive use of the ablated material was not clarified. In this report we present systematic investigations of spatial distribution of the laser ablation plasma in a wide variety of experimental parameters. It has been found that the maximum direction of the plasma expansion diagram is quite sensitive to the geometry of irradiation and much less sensitive to differences in physical characteristics of pairs of ablated materials and parameters of laser radiation. It has been demonstrated that even during simultaneous ablation of materials with significantly different atomic masses and mass removal rates, the maximum direction practically coincides with the symmetry axis of the system if it is aligned symmetrically. The angle width of the plasma diagram is rather small in both cases without and with a separating diaphragm, with an effective point plasma source localized at a few cm from the plane of the diaphragm on the target side. Time-of-flight measurements were conducted with two single probes in order to obtain energy distributions of ionized particles in the plasma. It has been found that mean energies are 1.5 times less and maximal energies in plasma are 2-3 times less as compared to the conventional PLD.

10:00-10:30

BREAK

SESSION II

Chairperson: M.C. Castex, Laboratoire de Physique des Lasers, Villetaneuse, France

G-II.1 10:30-11:00 - Invited -

IN-SITU MONITORING DURING PULSED LASER DEPOSITION, D.H.A. Blank, Low Temperature Division, Applied Physics, University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands

In Pulsed Laser Deposition (PLD) the diagnostics of the growing film surfaces by *in-situ* RHEED is hampered by the relatively high oxygen pressure. Therefore, several groups have monitored the growth of complex oxides with RHEED and have shown intensity oscillations, by depositing under low pressures compatible with their RHEED set-up.

However, the deposition pressure influences the size and shape of the plasma and, therefore, the deposition rate and the homogeneity of the thin film. In general the oxygen pressure is an important parameter in the oxidation process of the deposited film. The oxidation power is higher at higher pressures, which allows us to grow at higher deposition temperatures. This improves crystal structure of the deposited films. Moreover, some complex oxides, like high-Tc superconductors, are at high temperatures not stable in low oxygen pressure and, therefore, must be deposited at high oxygen pressures of up to 30 Pa to avoid decomposition of the film.

Here, an RHEED-PLD system is presented with which it is possible to monitor the growth at standard PLD-pressures. Results are shown of the two-dimensional growth of SrTiO_3 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and of layer by layer growth of ACuOx , with A=Sr, Ba, Ca. Furthermore, it is possible to monitor the crystallisation of the amount of material that is deposited by looking at the relaxations of the intensity after each laser pulse. This behaviour gives additional information about the mobility of the deposited material at the substrate temperature.

G-II.2 11:00-11:15

LASER-INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON-CARBON ALLOYS STUDIED BY ELECTRON MICROSCOPY AND RAMAN MICROSCOPY, C. Palma, M.C. Rossi*, C. Sapia*, E. Bemporad**, Departments of Physics, Electronic Engineering* and Industrial Mechanics**, University of Roma Tre, Via Vasca Navale 84, 00146 Roma, Italy

A strong interest is presently focused on laser crystallization of amorphous silicon. A fair understanding of basic crystallization in a-Si:H has been gained, whereas laser-induced photoeffects in amorphous alloys are less known. Moreover, crystallization processes in alloys induce phase-segregation effects. Here we present an investigation on the interaction between cw Ar^+ ion laser radiation and a- $\text{Si}_{1-x}\text{C}_x\text{H}$ films ($x=0.2-0.8$), reporting on structural and chemical changes as a function of both laser power density and alloy composition. It is shown that laser irradiation generally yields crystalline silicon, crystalline graphite and amorphous silicon carbide phases, while crystalline SiC phase can be obtained only under very particular conditions. Phase characterization and distribution in irradiated films is performed by scanning electron microscopy and Raman microspectroscopy. Information from experimental results is analyzed.

SYMPOSIUM G

G-II.3 11:15-11:30

PHOTODEFINED ETCHING OF n+ LAYERS DIFFUSED ON P-TYPE SILICON SUBSTRATES, R.S. Videira, R.M. Gamboa, J.M. Alves, J.M. Serra, A.M. Vallera; Dep. Fisica, Univ. de Lisboa, Campo Grande, 1700 Lisboa, Portugal

Non uniform n+ diffused layers on p-silicon are usually obtained by an uniform doping process followed by etch back in areas defined by a photolithographic mask applied onto the sample. We present here an alternative technique to obtain non uniform n+ doped layers using a photosensitive etching process, thus avoiding the photolithographic mask.

The electrochemical behaviour of silicon in HF (Hydrofluoric Acid), at a defined potential, is dependent on the illumination conditions and this allows the etching control imposing a light pattern on the sample surface. We present the general principles of this technique and the results of the application to n+ layers diffused on p type substrates. The results obtained so far show clearly that is possible to obtain photocontrolled etching. We also present a discussion on contrast limitations, based on experimental I(V) curves of the n+ layer in HF, measured on different stages of the etching process.

G-II.4 11:30-11:45

PULSED KrF LASER ANNEALING OF RF SPUTTERED ZnS:Mn THIN FILMS, E. Mastio, W.M. Cranton, C.B. Thomas, The Nottingham Trent University, Department of Electrical and Electronic Engineering, Burton Street, Nottingham NG1 4BU, UK and E. Fogarassy, S. de Unamuno, CNRS, Laboratoire PHASE (UPR du CNRS no. 292), BP 20, 67037 Strasbourg Cedex 2, France

Pulsed KrF laser annealing (LA) of ZnS:Mn thin (800nm) film phosphors is investigated as an alternative to thermal annealing for electroluminescent device fabrication. The influence of the surrounding gas pressure during irradiation, the energy density (Ed) of the laser beam and the effect of multiple shots is reported. Luminescent properties as function of laser energy density (Ed) are determined via photoluminescent (PL) characterisation. Energy densities used vary from 53 to 777 mJ/cm². PL intensities are determined to be linearly dependent with Ed beyond a threshold of 150 mJ/cm². Maximum PL enhancement at 777 mJ/cm² is a factor of 2.1x. A thermal simulation of the pulsed laser annealing process suggest that PL improvement is proportional to deposited thermal energy and confirms that at the maximum Ed no melting is occurring which is also in good agreement with previous work.

G-II.5 11:45-12:00

THICKNESS DEPENDENT PROPERTIES OF LaCaMnO THIN FILMS, R. Praus, B. Leibold, G.M. Gross and H.-U. Habermeier, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569, Stuttgart, Germany

Epitaxial thin films of La_{2/3}Ca_{1/3}MnO₃ (LCMO) were prepared by pulsed laser deposition (PLD) with SrTiO₃ (100) as substrate material. After the deposition the films were in situ annealed for one hour in oxygen (1 bar, 780°C). We studied the thickness dependence of the transport properties and the surface morphology in order to address the relation between the microscopic structure and the metal-insulator transition temperature T_{MI}. It could be demonstrated that T_{MI} decreases systematically from the bulk value T_{MI}=275 K with decreasing film thickness. Details of the temperature dependence of ρ and its magnetic field dependence will be discussed.

12:00-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III

Chairperson: R. Kelly, Dipart. di Fisica, Università di Trento, Povo (TN), Italy

G-III.1 14:00-14:30

NONTHERMAL EFFECTS DURING ArF LASER BEAM INTERACTION WITH BULK SILICON. FROM Si DESORPTION TO ABLATION, W. Marine, B. Kozlov, L. Patrone and M. Sentis, Groupement Interdisciplinaire Ablation Laser et Applications, UMR CNRS 6631 et UMR CNRS 6594, Faculté des Sciences de Luminy, Case 901, Marseille, France

We present new experimental studies of UV nanosecond pulsed laser desorption and ablation of (111) bulk silicon.

Nonthermal, photoinduced desorption of the surface atoms has been observed at low laser fluence, well below the melting threshold (0.5 J/cm²). The desorption flux is mostly composed of high energy ions with narrow energy distribution. The origin of these ions will be discussed on the basis of electronic excitation of Si surface states associated with Coulomb explosion mechanism.

The expansion dynamics of the ejected species has been analysed by reflectron time of flight mass spectrometry, optical spectroscopy and fast imaging set-up coupled with surface analysis by Atomic Force Microscopy. Under laser ablation condition, kinetic energy distributions and emission intensity of the ejected particles show that the nonthermal ions have high concentration and affect the dynamics of the laser induced plume expansion. This observation involves a new approach to analysis of the dynamics of the plume formation under high energy photon irradiation of the semiconductor surface.

G-III.2 14:30-14:45

FORMATION OF Ag NANOPARTICLES IN PULSED LASER DEPOSITED Ag-Ge ALLOYS, Z. Paszti, G. Peto, Z.E. Horvath, A. Karacs, MTA Research Institute for Technical Physics and Materials Science, 1525 Budapest, P.O.Box 49, Hungary and L. Guzzi, Department of Surface Chemistry and Catalysis, Institute of Isotopes, 1525 Budapest, P.O.Box 77, Hungary

The extremely high instantaneous deposition rate achievable by pulsed laser deposition makes this method suitable for preparation new metastable structures, such as alloys consisting of immiscible materials. In the present work we have investigated the electronic and atomic structure of pulsed laser deposited silver-germanium alloys with different silver contents between 1 and 30 atomic%. The samples were characterized by X-ray diffraction, transmission electron microscopy and photoelectron spectroscopy. The samples, according to the diffraction data, contain an amorphous silver-like phase, and diffraction patterns does not change after heat treatment up to 500 °C. On the other hand, the electronic structure data indicate that before any heat treatment silver is in the form of extremely small fine particles with electronic properties far from that of bulk but during heat treatment silver precipitates with more or less bulk-like electronic structure are formed. Thus, with suitable heat treatment of laser deposited metastable structures, it is possible to obtain granular materials containing precipitates with variable sizes in the nanometer range.

G-III.3 14:45-15:00

ON THE ORIGIN OF THE DIFFERENT VELOCITY PEAKS OF PARTICLES SPUTTERED FROM SURFACES BY LASER PULSES OR CHARGED BEAMS, A. Miotello and R. Kelly, Dipart. di Fisica, Università di Trento, Povo (TN), Italy

The particles emitted from surfaces irradiated by either laser pulses or charged-particle beams are often analyzed by time-of-flight (TOF) spectroscopy. This technique gives details on the velocity (thence energy) of the emitted particles, parameters which are of fundamental importance in establishing the mechanisms responsible for the particle emission. However, when experiments are performed in an ambient gas, primary effects may be partially obscured by collisions between the emitted particles and the ambient particles.

Here we will critically analyze the TOF spectra obtained when particles are sputtered from a surface. To this end we first discuss a variety of velocity laws in connection with the processes which create the different sputtered fluxes. We then compare results which led to two or more velocity peaks, considering in so doing ions, electrons, and laser pulses, as well as the absence or presence of ambient gas. In other words we try to establish simple criteria to distinguish primary emission mechanisms on the basis of TOF signals.

This subject is, unfortunately, not well developed in the contemporary literature.

G-III.4 15:00-15:15

EXPANSION DYNAMICS OF Bi ATOMS PRODUCED BY LASER ABLATION OF SINGLE AND MULTI-COMPONENT TARGETS, J. Gonzalo, J.M. Ballesteros and C.N. Afonso, Instituto de Optica (CSIC), Serrano 121, 28006 Madrid, Spain

The growth of good quality thin films by pulsed laser deposition requires the understanding of the expansion dynamics of the products present in the laser generated plasma. In this work, a comparative study of the expansion dynamics of Bi atoms and ions produced by laser ablation in vacuum of Bi₁₂GeO₂₀ and Bi targets has been carried out by spatially resolved real time optical emission spectroscopy.

In the case of ionized species, the emission features show no differences for both kind of targets; whereas for the neutral species ejected from the multi- component target, the emission lasts much longer and exhibits a two component expansion velocity distribution that could not be observed for single component targets.

The experimental results are discussed in terms of the existence of intraplume interaction processes that lead to the existence of a double population of neutrals in the case of the multi-component target.

G-III.5 15:15-15:30

CONDENSATION OF VAPOR AND NANOCLUSTERS FORMATION WITHIN THE VAPOR PLUME, PRODUCED BY NS-LASER ABLATION OF Si, B. Lukyanchuk, W. Marine, S. Anisimov

15:30-16:00

BREAK

SESSION IV

Chairperson: J. Perrière, Groupe de Physique des Solides, Universités Paris VII et VI, France

G-IV.1 16:00-16:30

LASER PROCESSING OF WIDE BAND GAP MATERIALS: ADVANCES IN DEPOSITION, ETCHING AND INTEGRATION OF NOVEL DEVICES, R.D. Vispute, V. Talyansky, S. Choopun, R. Enck, A. Balsamo, R.P. Sharma, and T. Venkatesan, CSR, Department of Physics, University of Maryland, College Park, MD, USA; A.A. Iliadis, Department of Electrical Engineering, University of Maryland, College Park MD, USA; K.A. Jones Army Research Laboratory, Adelphi, MD, USA

Materials processing utilizing lasers, especially high energy laser pulses have been widely adopted for the surface modification, annealing, cutting, welding, cleaning, etching, and deposition of ceramics, metals, and semiconductors. In my talk I will present our recent studies on the laser processing of the wide band gap III-V nitrides (AlGaIn) and ZnO that are currently the focal point of research in optoelectronics. Exploiting the laser-material interaction processes, we have developed a state of art pulsed laser deposition (PLD) technique for the growth of a variety of wide band gap metal-oxides and nitrides. We show that the crystalline and optical properties of the PLD GaN, AlN and ZnO films are comparable to those grown by MOCVD and MBE. The correlation of the processing variables with the structural, optical and electrical properties of the thin films will be discussed. We also discuss the laser processing of multilayer heterostructures for the integration of metal-oxides with III-V nitride technology, and the fabrication of novel optoelectronic devices. Further, the dry etching process based on the laser induced removal of the material has been employed for the etching of GaN and AlN films. It is observed that the etching mechanism is based on the laser induced absorption, decomposition, and layer by layer removal of the GaN.

G-IV.2 16:30-16:45

GROWTH MECHANISMS AND STRUCTURAL PROPERTIES OF PECVD SiO₂ FILMS DEPOSITED FROM O₂/TEOS PLASMAS IN A HELICON REACTOR, C. Vallée, A. Granier, A. Goullet, K. Aumaille, G. Turban, Laboratoire des Plasmas et des Couches Minces, IMN- CNRS-Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France

Silicon dioxide thin films are deposited at room temperature on silicon substrates in oxygen/tetraethoxysilane (O₂/TEOS) low pressure helicon diffusion plasmas. It was previously shown that stoichiometric films free from OH and C contaminants can be deposited in oxygen rich mixtures while SiO_xC_yH_z films are obtained in TEOS rich mixtures. The plasma is investigated by Optical Emission Spectroscopy (OES). The growth rate (Vd) and film properties are determined by in and ex situ spectroscopic ellipsometry (SE) measurements. Vd does not increase continuously with TEOS fraction in the mixture and presents a minimum value at 33% TEOS which corresponds to the transition from SiO₂H₂ to SiO_xC_yH_z films. This phenomenon, is partly explained by a competitive effect between deposition and etching, as evidenced by OES and SE. The minimum of Vd corresponds to the maximum of CO emission lines and a maximum value of the relative pressure increase in the plasma. The etching effect of carbon hydrogenated species by chemical reactions with O atoms is evidenced by post-exposure of the deposited film to pure O₂ plasma. Finally growth mechanisms in O₂/TEOS and Ar/TEOS plasmas are compared.

G-IV.3 16:45-17:00

EFFECTS OF PLASMA ON EXCIMER LAMP BASED SELECTIVE ACTIVATION PROCESSES FOR ELECTROLESS PLATING, D.J. Macauley, P.V. Kelly, K.F. Mongey and G.M. Crean, National Microelectronics Research Centre, Lee Maltings, Prospect Row, Cork, Ireland

A number of photosensitive activation processes for electroless plating have been reported in recent years using excimer lamps to selectively photodecompose various activation precursors. In this work, optical emission spectroscopy (OES) of a plasma existing in the process chamber during operation of a 222 nm KrCl* excimer lamp is presented. This plasma is shown to be generated by the excimer lamp power supply rather than by the 222 nm UV excimer lamp irradiation and is pressure dependent in the range from 4.0 x 10⁻⁴ mbar to atmospheric pressure. The effects of this plasma on previously reported photo-selective activation processes for electroless plating are discussed. A plasma assisted selective decomposition process is demonstrated. The effects of process chamber pressure as well as the N₂ gas fill on the plasma are also reported. Investigations into obtaining a selective activation for electroless metallisation in the absence of the plasma are also outlined. The copper metallisations achieved using a plasma assisted decomposition process are compared to those obtained using a true photodecomposition process.

G-IV.4 17:00-17:15

PULSED LASER DEPOSITION OF MULTICOMPONENT METAL AND OXIDE FILMS, M. Ozegowski, S. Metev, G. Sepold, Bremen Institute of Applied Beam Technology, Klagenfurter Str. 2, 28359 Bremen, Germany

Important deposition parameters of the PLD (Pulse Laser Deposition) technique like deposition rate, ion amount and kinetic ion energy are strongly determined by the laser parameters, especially by the laser wavelength and the laser power density. This was shown in this work by investigations of the pulsed plasma fluxes produced with four different lasers with wavelength from the UV (248 nm) to IR (10.6 μm) range. Herewith the possibility exists to adjust defined plasma parameters at the substrate by the choice of the laser parameters or also by a synchronous superposition of two different laser beams.

These results have been used to study the influence of the plasma parameters on the formation of a concrete thin film system consisting of a thin oxide layer (Al₂O₃) and a multicomponent metal alloy film (Cu-Mn-Ni). Oxide and metal films with a very smooth, nearly defect and droplet free surface could be synthesised by excimer laser. Deposition rates were in the order of 0.2 up to 1 Å per pulse. Films deposited with QS-Nd:YAG and TEA-CO₂ laser had a fine grained surface structure and some defects due to the presence of high energetic particles in the plasma flux.

Chemical composition, structure, adhesion, microhardness and elastic modulus of the films as well as functional properties of the film system were determined with different methods and correlated to the deposition conditions.

SYMPOSIUM G

G-IV.5 17:15-17:30

SENSITIZED IMPLANTATION OF FLUORESCENT MOLECULES IN POLYMER FILMS BY NEAR-INFRARED LASER IRRADIATION, H. Banjo, H. Fukumura, H. Masuhara, Osaka University, Suita, Osaka 565, Japan; N. Ichinose and S. Kawanishi, Japan Atomic Energy Research Institute, Neyagawa, Osaka 572, Japan

Functional organic molecules are potentially applicable toward building various kinds of molecular devices if the molecules can be fixed to a certain area of polymer surfaces. Such spatially selective implantation of molecules has been realized by using pulsed UV laser irradiation. Those molecules that absorb UV photons can convert electronic energy to thermal one and heat up the surrounding matrix, resulting in efficient diffusion of the molecules. This method has a disadvantage, however, since the molecules should be durable under intense UV laser irradiation. In this report, we present another method to implant molecules by adding near-IR sensitizer into the polymer matrix and relevant near-IR laser irradiation, instead of direct UV excitation of the molecules.

Fluorescence spectroscopy clearly showed that intact fluorescent molecules were implanted with the near-IR sensitization. The microcrystalline formation of those fluorescent molecules was found at the polymer surfaces by fluorescence microscopy. The microcrystalline was increased with the repetitive laser irradiation at the same surface, which was not observed in the case of UV irradiation. Thus some characteristics of the sensitized implantation were clarified and the underlying mechanism will be discussed in comparison with the direct UV excitation.

POSTER SESSION I

17:30-19:00

See programme of this poster session p. G-22 to p. G-29.

Wednesday June 17, 1998
 Mercredi 17 juin 1998

Afternoon
 Après-midi

SESSION V

Chairperson: M. Stuke, Max-Planck-Institut, Göttingen, Germany

- G-V.1** 14:00-14:30 - Invited - **DIFFRACTION LIMITED OPTICS FOR EXCIMER LASER BASED MICROPROCESSING**, H.-J. Kahlert and B. Burghardt, MicroLas Lasersystem GmbH, Robert-Bosch-Breite 10, 37079 Göttingen, Germany
 High resolution excimer laser based processing of material can be limited by process and material specific properties or by the resolution provided by the optics applied.
 Recent experiments with diffraction limited projection lenses have demonstrated that excimer laser based processing at high resolution further is sensitive on the spatial coherent of the laser beam and on the partial coherence of the projection lens' illumination.
 The experiments were performed with a MicroLas 5x/18-248 diffraction limited projection lens with a NA=0.13 (resolution limit 1-2µm) with a 100 W 248nm excimer laser (NovaLine 100). Experimental results will be presented and compared to theoretical models.
- G-V.2** 14:30-14:45 **MICRODEPOSITION AND MICROETCHING OF DIFFRACTIVE STRUCTURES USING ULTRASHORT LASER PULSES**, I. Zergioti**, S. Mailis, N.A. Vainos, A. Ikiades, C.P. Grigoropoulos*, and C. Fotakis, Foundation for Research and Technology-Hellas, FORTH-IESL, P.O. Box 1527, 71110 Hellas, Greece; *Department of Mechanical Engineering, University of California, Berkeley CA 94720, USA; **Present address: Max-Planck Institut für biophysikalische Chemie, P.O. Box 2841, 37018 Göttingen, Germany
 Two complementary methods, the microetching and the microdeposition, of materials using ultrashort pulses of ultraviolet laser radiation for the fabrication of diffractive structures are presented. Microetching of various solid materials (polymers, metals) using fs excimer lasers produces high definition micron diffractive patterns. The microdeposition method utilizes the selective microablation and transfer of thin metallic films for achieving microstructures of dots, lines and complicated multilevel patterns with micron and even submicron resolution. The short pulse length and the consequent limited thermal diffusion, lowers the ablation threshold and enables the machining and the deposition of high definition features. The superior quality of the results allows the direct, in-one-step process, fabrication of binary amplitude and multilevel optical diffractive structures on planar and cylindrical substrates such as optical fibres.
- G-V.3** 14:45-15:00 **PHOTOPOLYMERIZATION BY EVANESCENT WAVES: A NEW METHOD TO OBTAIN NANOMETRIC FILMS OF PHOTOPOLYMER**, A. Espanet, C. Ecoffet and D.J. Lougnot, Laboratoire de Photochimie Générale, CNRS-UMR7525, 3 rue Alfred Werner, 68093 Mulhouse, France
 A new procedure for the gelation of a thin layer of a photopolymerizable formulation is presented: photopolymerization by evanescent waves (PEW). In this procedure, the area of interaction of the actinic light with the reactive formulation is confined within a layer of few hundreds of nanometers. The confinement of the light is achieved by Total Internal Reflection (TIR) of the light at the interface between the material and an high index prism. This method is particularly suitable for the fabrication of micro parts and thin films (30 to 800 nm).
 A simplistic model was proposed to connect polymerized thickness with photonic and optical parameters. The analysis of the experimental results lets appear slight discrepancies with this model. That can be interpreted in terms of modifications of the optical properties of the material and of competition between reaction processes and diffusion of the molecules.
- G-V.4** 15:00-15:15 **MODIFICATIONS OF POLYETHER-ETHERKETONE SURFACE AFTER 193 NM AND 248 NM EXCIMER LASER RADIATIONS**, P. Laurens and B. Sadras, CLFA, 16 bis av. Prieur de la Côte d'Or, 94114 Arcueil, France, Fr. Decobert, CREA/MSA, 16 bis av. Prieur de la Côte d'Or, 94114 Arcueil cedex, France; F. Arefi and J. Amouroux, Laboratoire des Réacteurs Plasmas, ENSCP, 11 rue P. et M. Curie, 75231 Paris cedex, France
 The modifications induced by excimer laser irradiation on PEEK surfaces have been investigated depending on the laser process parameters for laser fluences below the material ablation threshold. Treated PEEK surfaces were characterized by SEM, TEM, XPS, surface wettability and adhesive bonding test. Results shows that the PEEK surface modifications and adhesive properties first depended on the laser wavelength. In the case of an 193 nm laser treatment, a tremendous increase of the adhesive properties of PEEK can be obtained. This increase is related to the formation of new reactive groups on the treated surface (hydroxyl, carboxyl groups) that induce an acidic character on the surface which favors wetting and adhesion with a basic epoxy adhesive. The content of these reactive groups has to be controlled since their presence in high concentration may also have a negative effect on the mechanical properties of the treated surface. On the contrary, laser treatment using a 248 nm radiation never lead to a significant increase in the adhesive bonding properties of PEEK. This has to be related to the lack of reactive groups on the modified surface but also to a possible weakening on the surface mechanical properties induced at this laser wavelength.

SYMPOSIUM G

G-V.5 15:15-15:30

VUV LASER PROCESSING OF POLYMERS AT 10 eV, D. Riedel, M.C. Castex, Laboratoire de Physique des Lasers, Université Paris-Nord, Av. J.B. Clément, 93430 Villetaneuse, France

Polymers are key materials in new technologies owing to their exceptional properties. In most applications the key point concerns the treatment and the control of polymer film's surfaces and interfaces. An attractive approach may be found by using a VUV laser. Efficient coupling between light and matter is expected: any polymer can be treated and surface structuration can be realized with submicron spatial resolution. Demonstration is given here, for the first time, that efficient and clean etching of different polymers (PTFE, PMMA) can be achieved at 10 eV with a pulsed VUV coherent source, obtained by four-wave mixing $2\omega_w + \omega_{vis}$ in mercury vapour at room temperature [1]. Moreover, the experimental set-up is convenient for comparative laser studies at three different wavelengths 626, 313 and 125 nm. Compared to the clean etching of PMMA at 125 nm, thermal degradation is indeed observed at 313 nm.

Evolution of etch rates for PTFE and PMMA have been measured as a function of the 10 eV laser fluence in the range 1 to 1000 mJ/cm². They follow a logarithmic fluence dependence representative of an absorption Beer-Lambert's law with threshold values as low as 1 mJ/cm². The high effective absorption coefficients measured demonstrate the efficiency of the VUV laser/surface coupling with penetration depth < 1 nm [2]. In addition, time and spectrally resolved luminescence is used as a probe of polymer surface qualities and transformation.

[1] L. Muscur, W.Q. Zheng, A. Kanaev and M.C. Castex, IEEE Sel.Top QE 1, 900 (1995)

[2] D. Riedel and M.C. Castex, SPIE "Advanced Laser technologies" to be published

15:30-16:00

BREAK

G-V.6 16:00-16:30 - Invited -

AN UPDATING OF THE PROBLEM OF THERMAL MECHANISMS OF PULSED-LASER SPUTTERING, R. Kelly and A. Miotello, Dipart. di Fisica, Università di Trento, Povo (TN), Italy

There are basically 4 mechanisms of pulsed-laser sputtering that could be termed thermal. These involve, respectively, (a) normal vaporization in accordance with the Hertz-Knudsen equation, (b) normal boiling, i.e. boiling based on heterogeneous nuclei, (c) phase explosion, which is effectively target disintegration in the vicinity of T_{ic} (the thermodynamic critical temperature), and (d) subsurface heating.

What we term "normal vaporization" in general gives no problem as it is precisely calculable in terms of the Hertz-Knudsen equation. But the appropriate thermodynamic information often lacks.

"Normal boiling" is difficult to quantify. While heterogeneous nuclei in the conventional sense are too few to be relevant, the surface could serve as a nucleating center. At this point we need information on the size of the nuclei. For example, if the nuclei are small enough then they will diffuse to the surface, but one asks whether the diffusion velocity is sufficient. "Phase explosion" involves homogeneous nuclei. There are here two problems. One is that the nucleation has a time constant of order 1-100 ns and the other is the question of whether the nuclei move or whether the nucleated volume simply disintegrates. What we term "sub-surface heating" is the simplest to discuss. The current literature notwithstanding, it simply does not exist!

G-V.7 16:30-16:45

MONTE CARLO SIMULATION OF THE LASER-INDUCED PLASMA PLUME EXPANSION UNDER VACUUM AND BACKGROUND GASES, F. Garrelie, J. Aubreton and A. Catherinot, LMCTS-PLM, Faculté des Sciences, 123 Av. A. Thomas, 87060 Limoges, France

The plasma plume expansion created by pulsed laser irradiation of a copper target at high laser fluence, when more than few monolayers of materials are evaporated, has been theoretically investigated by means of a Monte Carlo simulation.

The simulation shows that the expansion under vacuum of laser ablated particles is dominated by the laser energy absorption by the evaporated particles during the laser pulse duration. A comparison between simulated time of flight curves and experimental curves obtained by spectroscopic time of flight has shown that about 6% of the incoming laser energy was contributing to the expansion processes through the time-delayed recombination of this energy into kinetic energy. The expansion of a fully thermalized plasma plume has been found to be very different from experimentally observable expansion.

The plasma plume expansion under a residual argon pressure of few mbar has been found to be very affected by collisions between laser ablated and ambient gas particles. The high density region in the plume appears to be deficient in background gas particles, whereas a snowplow of the ejected particles in the leading edge of the plume is observed due to the compression of the ambient gas around the laser-induced plasma plume.

G-V.8 16:45-17:00

TIME OF FLIGHT ANALYSIS OF LASER-INDUCED PROCESSING IN SAPPHIRE WITH ULTRA-SHORT PULSES, R. Stoian, H. Varel, A. Rosenfeld, D. Ashkenasi and E.E.B. Campbell, Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, PF. 1107, 12474 Berlin-Adlershof, Germany

Recent time-resolved pump-probe studies on the ablation of several dielectrics during laser-induced surface modification with 100 femtosecond laser pulses at 800 nm demonstrated an early beginning of material removal. The ablation process starts only 2 ps for amorphous and crystalline SiO₂ and 20 ps for sapphire after surface excitation. For investigations on the ablation mechanism it is essential to avoid any laser-plume interaction, otherwise severely complicating the problem. This confines the pulse-width range to a few picoseconds. Sapphire is a most interesting candidate, since it exhibits two completely different etch phases. Corresponding to the ex-situ analysis of the modifications we performed time-of-flight (TOF) measurements of the ablation process. First results in the velocity distributions of the Al⁺ and O⁺ ions seem to indicate that a second high velocity peak develops for both constituents at the point, where we observe ex-situ the transition from the gentle to the strong etch phase. We therefore greatly extended our TOF measurements, investigating the velocity and angular distribution of the ions in the plume. The results will be presented in dependence of the laser intensity, laser wavelength and number of laser pulses. We will discuss the different nature of the ablation mechanism in sapphire on the basis of our mass selective and time resolved investigations.

SYMPOSIUM G

G-V.9 17:00-17:15

MODELING OF VELOCITY AND SURFACE TEMPERATURE OF THE MOVING INTERFACE DURING LASER ABLATION OF POLYIMIDE AND POLYMETHYL-METHACRYLATE, H. Schmidt*, J. Ihlemann, Laser-Laboratorium Göttingen, PO Box 2619, 37016 Göttingen, Germany; K. Luther, J. Troe, Inst. f. Phys. Chem., Univ. Göttingen, Tammannstr. 6, 37077 Göttingen, Germany, * present address: MicroLas Lasersystem GmbH, Robert-Bosch-Breite 10, 37079 Göttingen, Germany

A model, which agrees with extensive measurements of pulse duration and spot size dependence of nanosecond laser ablation rates of polyimide (PI) and polymethyl-methacrylate (PMMA) [1], is applied to calculate the temporal behavior of position (velocity) and temperature of the sample surface ("moving interface") during ablation at 308 nm and 248 nm. The polymer is described as a system of chromophores with two electronic states. Photochemical decomposition and photodissociative bond breaking in the excited state are possible. Laser induced chemical modifications are incorporated via different absorptivities for initial and UV-modified polymer. Dynamic attenuation of the expanding ablation plume and heat conduction are taken into account.

Maximum surface temperatures during ablation of about 3000 K (PI) and 700 K (PMMA) are predicted. Typical maximum velocities of the moving interface range from 20 m/s (PI) to 100 m/s (PMMA) for a pulse duration of 20 ns at a fluence of 4 J/cm². The calculated plume transmission data support the significance of lateral plume expansion for the increase of ablation rates with growing pulse duration and decreasing laser spot size.

[1] H. Schmidt, J. Ihlemann, B. Wolff-Rottke, K. Luther, J. Troe, J. Appl. Phys., May 1998.

G-V.10 17:15-17:30

SUB- μ m GRATING FORMATION IN Ta₂O₅-WAVEGUIDES BY FEMTOSECOND UV-LASER ABLATION, F. Beinhorn, J. Ihlemann, P. Simon, G. Marowsky, Laser-Laboratorium Göttingen e.V., PO Box 2619, 37016 Göttingen, Germany; B. Maisenhölder, J. Edlinger, Balzers Thin Films, 9496 Balzers, Liechtenstein, D. Neuschäfer, D. Anselmetti, Novartis AG, 4002 Basel, Switzerland

Sub-micron surface gratings on Ta₂O₅ waveguide layers were produced by ablation with a sub-ps-UV-laser. The structure is generated by projection imaging of a primary transmission grating mask. A grating of 500 nm period with a surface modulation depth of 10 nm on a sample area of about 300 μ m x 300 μ m can be produced with a single laser pulse of about 100 mJ/cm² at 248 nm wavelength. Adjustment of the modulation depth to specific requirements can be accomplished by varying laser fluence or pulse number. The gratings show good coupling efficiency.

POSTER SESSION II

17:30-19:00

See programme of this poster session p. G-30 to p. G-37.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VI

Chairperson: D.H.A. Blank, Low Temperature Division, University of Twente, The Netherlands

G-VI.1 8:30-9:00 - Invited -

J. Chung, POSTECH, Pohang, Korea

G-VI.2 9:00-9:15

HIGH DENSITY PLASMA ETCHING OF NiFe, NiFeCo And NiMnSb-BASED MULTILAYERS FOR MAGNETIC STORAGE ELEMENTS, K.B. Jung, J. Hong, J.A. Caballero, J.R. Childress, S.J. Pearton, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA and M. Jenson and A.T. Hurst, Jr., Honeywell Solid State Electronics Center, Plymouth MN 55441, USA

Magnetic multilayer thin films based on the Giant Magnetoresistive effect are the basis of extremely high density (>10 Gbit-in⁻²) data storage systems. A challenge to continue the rapid growth in bit density is the ability to pattern sub-micron features in materials such as Ni_{0.8}Fe_{0.2}, NiFeCo alloys and NiMnSb. Conventional reactive ion etching methods are generally unable to successfully etch these materials because of the low volatility of the etch products. We have found that Electron Cyclotron Resonance and Inductively Coupled Plasma sources operating with ion densities several orders of magnitude higher than RIE provide etch rates of 2000-5000 Å·min⁻¹ for NiFe and NiFeCo in Cl₂/Ar discharges, and $>10,000$ Å·min⁻¹ for NiMnSb in SF₆/Ar or NF₃/Ar. Sub-micron features with smooth, vertical sidewalls are obtained using SiO₂ or SiN_x masks. Photoresist is generally found to be an unsuitable mask under high density plasma conditions. Post-etch cleaning of chlorine residues in H₂ or O₂ in-situ plasmas is effective in avoiding sidewall corrosion.

G-VI.3 9:15-9:30

FIRST CHEVREL-PHASES COMPOUNDS EPITAXIALLY GROWN BY PULSED LASER DEPOSITION, X. Guilloux-Viry, N. Lemée, A. Perrin, LCSIM, UMR CNRS 6511, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

Pulsed Laser Deposition (PLD) appears as a very versatile method. As an illustration, molybdenum cluster sulfides thin films have been in-situ deposited for the first time by PLD. This method has allowed the first epitaxial growth of Chevrel-phases, for instance of Cu_xMo₆S₈. PLD enabled us to grow these sulfides under secondary vacuum and also to decrease the synthesis temperature.

These films, grown on R-plane Al₂O₃ with the (100)_R preferential orientation, present an original in-plane double epitaxy, related to unit cell symmetries, as shown by XRD diagrams (θ -2 θ , ϕ -scans) and RHEED patterns which consist in narrow streaks.

Smooth films have been obtained, presenting good superconducting properties in agreement with the structural characteristics, i.e. narrow transitions with T_c ~ 10 K, depending on copper content, comparable to bulk behaviour.

G-VI.4 9:30-9:45

OXIDE FILMS DEPOSITED BY REACTIVE PULSED LASER ABLATION, A. Mele, C. Flamini, Dipart. di Chimica, Univ. "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy; R. Teghil, Dipart. di Chimica, Univ. della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy; S. Orlando, V. Marotta, Istituto Materiali Speciali CNR, 85051 Tito Scalo (Pz), Italy

The deposition of oxide films has becoming an increasing important area of technological interest due their numerous applications in different fields. Metal oxide coatings are widely used, for example, as antireflecting and high index materials for optical applications or diffusion barriers in microelectronics as well as protective layers against aggressive media. Simple oxides as TiO₂, ZrO₂, SiO₂ have been deposited by Pulsed Laser Ablation and Deposition (PLAD) technique. The thin films, deposited on Si(100), Si(111) and polymeric substrates, have been characterized by Scanning and Transmission Electron Microscopy (SEM and TEM), X-Ray Diffraction analysis (XRD), X-Ray Photoelectron Spectroscopy (XPS), and scratch tests. Refractive index is measured. Furthermore a Intensified Charge Coupled Device (ICCD) camera and a optical Multichannel Analyzer have been used to investigate the plume expansion and composition. Laser fluence, buffer gas presence, and geometrical parameters of deposition have been optimized to improve the technological characteristics of the deposited films.

G-VI.5 9:45-10:00

CN_x FILMS DEPOSITED BY INTRODUCTION OF GRAPHITE INTO AN EXPANDING Ar/N₂ PLASMA, A. de Graaf, P.D.J. van Deurzen, M.C.M. van de Sanden, D.C. Schram, Eindhoven University of Technology, Department of Applied Physics, PO Box 513, 5600 MB Eindhoven, The Netherlands and E. Aldea, G. Dinescu, National Institute of Lasers, Plasma and Radiation Physics, Low Temperature Plasma Department, PO Box MG 36, Bucharest-Magurele, Romania

In the synthesis of good-quality carbon nitride, a material with a predicted hardness comparable to that of diamond, incorporation of hydrogen should be avoided. Therefore, for deposition of this compound hydrogen-free carbon precursors have to be sought. The method described here makes use of a graphite nozzle through which an Ar/N₂ plasma is expanding. It is shown that the graphite is sputtered by the Ar/N₂ plasma and that the sputtering is chemical rather than physical. The plasma is investigated by means of Optical Emission Spectroscopy (OES), and the film growth is monitored by in situ ellipsometry. The growth rate increases with increasing nitrogen concentration in the plasma and is proportional to the emission of the B²Σ → A²Π CN-band. The emission of the N₂⁺ B²Σ → X²Σ band and the B²Σ → A²Π CN-band is also used to determine the rotational and vibrational temperature in the plasma. These temperatures are compared to the rovibrational temperatures found in a pure Ar/N₂ plasma and the electron temperature as measured with Langmuir probe.

10:00-10:30

BREAK

SESSION VII

Chairperson: I. Zergioti, Max-Planck-Institut, Göttingen, Germany

G-VII.1 10:30-11:00 - Invited -

UTILIZATION OF Cu(HFAC)TMVS PRECURSOR GAS IN LCVD INTEGRATED CIRCUIT REPAIR SYSTEM, S. Leppävuori, J. Remes, H. Moilanen, Microelectronics Laboratory, EMPART Research Group of Infotech Oulu, University of Oulu, 90570 Oulu, Finland

Various techniques have been developed in order to carry out integrated circuit repairs during IC prototyping. Focused ion beam (FIB) etching and deposition is for the time being the most powerful and versatile tool for multilevel IC modification and failure analysis but a long distance conductor line deposition with an acceptable electrical resistance is time consuming.

Laser chemical vapor deposition (LCVD) has not such a high accuracy but the bulk resistivity metal deposition over large areas and long distances is carried out in seconds.

In this work LCVD of copper from Cu(hfac)tmvs is shown to be applicable for actual integrated circuit repair work. Several examples including signal rewires, probing and bonding pads as well as large area copper deposition are presented in this work. The deposition morphology and chemical contents are studied by AFM and LIMA measurements, respectively. During Cu deposition the precursor container was heated to a temperature of 36 °C resulting in 0.3 mbar partial pressure in the chamber. A typical flow rate of the Cu(hfac)tmvs precursor was set to 2.0 sccm and the total pressure in the chamber was adjusted between 5 to 10 mbar. Ar⁺ laser, employing mainly the peaks at 488 nm and 515 nm was utilised with scan speed 24 µm/s. The resistivity of the deposited lines was found to be 2.7 µΩcm.

G-VII.2 11:00-11:15

EXCIMER LASER ABLATION OF MOLTEN METALS AS FOLLOWED BY ULTRAFAST PHOTOGRAPHY, Z. Toth, B. Hopp, Z. Kantor*, F. Ignacz, T. Szörényi and Z. Bor*, Research Group on Laser Physics of the Hungarian Academy of Sciences, *Department of Optics and Quantum Electronics, Jozsef Attila University, POB 406, Szeged, 6701, Hungary

The use of liquid targets in pulsed laser deposition is a straightforward approach to reduce the number of particulates. Although droplet formation can not completely be eliminated, metal films deposited from liquid targets contain much less particulates as compared to the solid-target case. The aim of this study is to unveil the processes leading to droplet emission from the ablated target surface. Molten indium was ablated in vacuum by an ArF excimer laser. Pictures of the surface and the ablated material were taken at different moments after the start of the excimer laser pulse by ultrafast photography with temporal resolution of 1 ns using delayed dye laser pulses. The series of snapshots contain information on the initial stage of droplet formation, the shape of the surface waves and the vibrations of the whole melt pool disturbed by the mechanical effects upon ablation. The measurement of the recovery time of the flat liquid surface is important in determining the necessary delay between consecutive ablating pulses to ensure ablation of an already relaxed surface.

G-VII.3 11:15-11:30

UV LASER POLISHING OF THICK DIAMOND FILMS FOR IR WINDOWS, S. Gloor, W. Lüthy, H.P. Weber, Institute of Applied Physics, Sidlerstr. 5, 3012 Berne, Switzerland; S.M. Pimenov, V.G. Ralchenko, V.I. Konov, General Physics Institute, 38 Vavilov Street, 117942 Moscow, Russia and A.V. Khomich, Institute of Radio Engineering & Electronics, Ac. Vvedensky Sq.1, 141120 Fryazino, Moscow Region, Russia

Diamond has very suitable properties for infrared (IR) window applications. The rugged surface of a free-standing 320 µm thick diamond film grown by chemical vapor deposition (CVD) is polished with the UV light of an ArF excimer laser ($\lambda = 193$). The angle of incidence is 85° and irradiation is performed from three directions. Scanning electron microscopy (SEM) is used to visualize the surface before and after the polishing procedure. With a profilometer (tip radius 5 µm) the improvement of the average roughness of the surface is measured. Polishing is analyzed in dependence on the size of surface irregularities by means of fast Fourier transformation (FFT) of the signal of the profilometer. Surface roughness measurements are also performed on the polished surface with an atomic force microscope (AFM). With IR transmission measurements the optical quality is analyzed over a wavelength range of 2.5 to 25 µm before and after polishing. The oxidative removal of the laser induced graphitic layer is studied with optical spectroscopy techniques.

G-VII.4 11:30-11:45

LASER CLEANING OF TINY PARTICLES IN A THIN LIQUID LAYER AND ITS THEORETICAL MODEL, Y.F. Lu, Y. Zhang and W.D. Song, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, 119260 Singapore

The microparticles can be removed from nickel-phosphorus (NiP) surface through laser cleaning with deposition of a thin liquid film. The optical micrograph and AFM were used to observe the NiP surface before and after laser cleaning. It is shown that the cleaning efficiency increases quickly with increasing of laser fluence. The cleaning threshold of laser fluence for small particles is larger than that for large particles.

A theoretical model is established by taking adhesion force and cleaning force into account. When pulsed laser irradiates on the solid surface coated with a thin liquid film, a sheet of liquid near the liquid/substrate interface can be superheated through thermal diffusion. The rapid growth of vapor bubbles inside the superheated liquid can generate transient stress wave with high pressure, large enough to expel micron and sub-micron particles from the contaminated surface. Through calculating adhesion force and cleaning force, the cleaning threshold of laser fluence can be predicted from this theoretical model and the results indicate that small particles have larger cleaning threshold than large particles.

SYMPOSIUM G

G-VII.5 11:45-12:00

EFFECTS OF COBALT THIN FILMS ON THE a-Si CRYSTALLISATION INDUCED BY EXCIMER LASER IRRADIATION, S. Luby, Slovak Academy of Sciences; G. Leggieri, University of Lecce, Italy and P. Mengucci, University of Ancona, Italy
Large grains polycrystalline silicon is intensely studied for applications in semiconductor devices and circuits. So, different methods have been developed to deposit poly-Si layer and in particular to improve the crystallinity of the Si layers deposited onto amorphous substrates. In this respect, however, metal ultrathin layers inducing islands-like or continuous nucleation under laser irradiation have never been used up to now. In the present work we report the results obtained by laser irradiation of a-Si/Co/SiO₂ and a-Si/SiO₂ samples in order to study the influence of the Co film on the a-Si crystallisation process. Samples were irradiated by a XeCl excimer laser under different fluence and pulse numbers. Grazing angle XRD and cross sectional TEM were used for sample characterisation. Results showed the formation of CoSi₂ that, in general, considerably improves the crystallinity of the a-Si layer. In some cases the presence of the CoSi₂ underlayer allowed the complete crystallisation of the a-Si layer even after the first laser pulse. Without CoSi₂ the same results were obtained only with a higher number of pulses.

12:00-14:00

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION VIII

Chairperson: A. Catherinot, Université de Limoges, France

G-VIII.1 14:00-14:30

MAGNETIC FIELD ASSISTED PULSED LASER DEPOSITION, C. de Julian Fernandez, J.L. Vassent and D. Givord, Laboratoire Louis Néel, CNRS, BP 166, 38042-Grenoble-Cedex, France

Pulsed Laser Deposition has been used in the last few years for film preparation of various materials. In this technique, the plasma plume of evaporated species contains a large fraction of ions. We will show that i) by applying an "axial" static magnetic field (field direction, z, perpendicular to the target surface) of approximately 0.2 T on the plume, it is possible to force the expansion of the plume along z, and thus concentrate the deposition in a substrate region which is much more restricted than in the absence of a field, ii) by applying a transverse field (perpendicular to z) of the same order of magnitude, it is possible to deviate the plume into the field direction.

An original PLD cylindrical chamber has been built in which axial and transverse fields are combined. The direction of the transverse field may be rotated about the z-axis. This allows free-droplet films to be deposited on six specified substrates which are arranged on the chamber inner diameter. Eight different targets are arranged on a drum which rotates at 10 rpm. The laser delivers pulses at 10Hz and these are synchronised with target rotation. Multi-element films may thus be prepared by mixing the target elements on a one to one laser pulse basis. The properties of various materials prepared will be presented to illustrate the potential of this original set-up.

G-VIII.2 14:30-14:45

NITRIDING WITH ION BEAM FROM HALL TYPE SOURCE, M. Bacal, Laboratoire P.M.I., UMR 7648 du C.N.R.S., Ecole Polytechnique, 91128 Palaiseau, France and J-P. Peyre, C.E.T.I.M., 52, avenue Felix-Louat, B.P. 80067, 60304 Senlis, France

The nitrogen ion beam produced by a Hall type ion source has been used for the nitriding of 34CrMo4 steel, in order to evaluate the potential of this device for surface processing. This compact device combines an ion source and an accelerator. It provides a very high ion current density because the ion space charge is neutralized by the closed cycle electron drift. The ion energy at the exit of the discharge channel is close to the discharge voltage.

The nitriding was performed at two temperatures: 570°C and 350°C. The duration of the nitriding was 4 hours in the first case and 8 hours in the second one. At 350°C the combination film was 2-3 µm thick and the diffusion film was 150 µm thick. The maximum hardness on the surface is 671 HV0.05. The results indicate that the new method employed allows faster nitriding kinetics and lower sample temperature than the conventional ones. The method appears to be highly directional.

The support of the European Commission within INCO-COPERNICUS Project (contract IC15CT960730) is acknowledged.

G-VIII.3 14:45-15:00

LASER ASSISTED CVD OF BORON CARBIDE AT ATMOSPHERIC PRESSURE, J.C. Oliveira, P. Paiva, M.N. Oliveira and O. Conde, Physics Department, University of Lisbon, Campo Grande, Ed. C1, 1700 Lisboa, Portugal

In a previous study, laser assisted chemical vapour deposition of boron carbide thin films was successfully carried out from a gas mixture of BC13, CH4, H2 and Ar at working pressure of 133 mbar, using a cw CO2 laser. This paper focuses on the deposition of rhombohedral boron carbide at atmospheric pressure from the same precursor gases. Laser assisted deposition at atmospheric pressure is an interesting process for industrial applications since there is no need for high vacuum systems and it allows easy automation and continuous high-rate coating to be performed.

Raman microprobe spectroscopy and X-ray diffraction were used for structural characterisation of the coatings. The chemical composition was determined by electron probe microanalysis and the morphology was investigated by scanning electron microscopy. The deposition of single phase boron carbide films with shiny grey colour and crystalline morphology was achieved at laser irradiances under 90 W/cm2. At higher irradiance values, unlike deposition at lower pressure, the films present a dark central region with whisker-like morphology consisting of a mixture of boron carbide and disordered graphite.

G-VIII.4 15:00-15:15

DEPOSITION OF CRYSTALLINE TEFLON THIN FILMS BY VUV RADIATION PHOTODECOMPOSITION, T. Katoh and Y. Zhang, Sumitomo Heavy Industries, Ltd., 2-1-1 Yatocho, Tanashi, Tokyo 188, Japan

Crystalline thin films of Teflon (polytetrafluoroethylene) was deposited on Si (100) substrates by VUV irradiation (Photon flux on the sample surface was on the order of a few 10^{17} photons/s cm²) of a Teflon target in vacuum. An increase in the target temperature made great improvements including considerable enhancement of the deposition rates, reduction of the CF₃ component and achievement of the crystalline features closer to the Teflon target, whereas an increase in the substrate temperature made the film surface rough. The maximum deposition rate was about 20 nm/s, much higher than 0.1-1 nm/s by the vacuum pyrolysis and 0.4 nm/s by the F₂ laser ablation (assume a repetition rate of 50 Hz). X-ray photoelectron spectroscopy (XPS) analysis of the deposited films showed that F/C=2.01-2.10, slightly larger than 1.95 of the target materials; both Fourier transfer infrared (FTIR) and x-ray diffraction (XRD) analyses showed that there is CF₃ component; quadrupole mass spectrometric analysis showed that the main ion signal was CF₃⁺ (69 amu) due to saturated fluorocarbons. Based on the above analyses, we believed that, different from the laser ablation of Teflon for the deposition, the VUV-induced reactions should be ablative photochemical decomposition (APD) rather than photo-thermal unzipping decomposition, yielding saturated fluorocarbons rather than monomers as the main gaseous products. Further studies on the etching rate showed that there is no threshold in photon flux, so the VUV irradiation of the Teflon should be a direct photo-etching process rather than the ablation process which powerful laser does. The decomposition process can be applied not only to deposition of the crystalline Teflon films but also to micromachining of the Teflon to creating microstructures with very high aspect-ratios.

SYMPOSIUM G

G-VIII.5 15:15-15:30

UV LASER SURFACE PROCESSING OF METALLIC ALLOYS: COMPARISON OF EXPERIMENTAL AND NUMERICAL RESULTS, G. Nicolas, A. Yanez, A. Ramil, J.C. Alvarez, E. Saavedra, Escuela Politecnica Superior, Universidad de La Coruna, C/Mendizabal s/n, 15403 Ferrol, Spain; J.L. Ocana, A. Garcia-Beltran, C. Molpeceres, ETSIIMLAS Dpto de Fisica Aplicada (U.P.M.), C/ Jose Gutierrez Abascal 2, 28006 Madrid, Spain; M. Autric, IRPHE, Laboratoire LP3, 163 Av. de Luminy, 13009 Marseille, France

The modifications resulting from a laser irradiation and which occur in solid materials are located mainly in the near surface region. An examination of the exposed areas and cross sections allows to determine the influence of such a treatment.

For most of materials, a molten layer is formed during the interaction processes and its depth depends on the irradiation conditions. The thickness of this layer can be measured experimentally but can also be predicted by a numerical modelling which provides an analysis of the thermal cycles developed into the sample.

In the present study, a KrF laser radiation has been used to irradiate metallic alloys in air and experimental and numerical investigations have been performed in order to compare both results.

The aim is to provide complementary information for a more complete understanding of the complex phenomena involved in the interaction : propagation of melt front into solid and vaporisation/plasma expansion in the surrounding atmosphere.

15:30-16:00

BREAK

SESSION IX

Chairperson: J. Perrière, Groupe de Physique des Solides, Universités Paris VII et VI, France

G-IX.1 16:00-16:30

EXCIMER LASER IRRADIATION INDUCED FORMATION OF DIAMOND-LIKE CARBON LAYER ON GRAPHITE, A. Mechler, P. Heszler*, Z. Kantor, T. Szörényi* and Z. Bor, Department of Optics and Quantum Electronics, Jozsef Attila University, *Research Group on Laser Physics of the Hungarian Academy of Sciences, POB 406, Szeged 6701, Hungary

Graphite targets are generally used in pulsed laser deposition as sources for diamond and diamond-like carbon (DLC) film growth. The majority of the reports concentrates on the properties of the ablated material and the deposited thin films. We focus on the changes of the target surface due to excimer laser processing.

Highly oriented pyrolytic graphite (HOPG) surfaces were irradiated with ArF excimer laser ($\lambda = 193$ nm) pulses of 2 J/cm^2 . The depth of the hole produced by the first laser shot was 75 nm, while subsequent pulses resulted in a further increase of approx. 10 nm only, revealing that subsequent pulses impinge on a different material. Area-selective Raman spectroscopy and atomic force microscopic (AFM) measurements revealed that an approx. 300 nm thick hydrogen-free diamond-like carbon layer was formed on the surface. The density of this DLC layer is approx. 2.8 g/cm^3 and the proportion of the sp^3 hybrid-states of carbon is approx. 50 %. Annealing in air at 650°C for 30 minutes recovers the graphite structure.

G-IX.2 16:30-16:45

LIQUID CRYSTAL FILMS GROWN BY PULSED LASER DEPOSITION, J. Gonzalo, P.E. Dyer, H.V. Snelling, Department of Physics, University of Hull, Hull HU6 7RX, UK and M. Hird, Department of Chemistry, University of Hull, Hull HU6 7RX, UK

Pulsed laser ablation deposition is a potentially interesting method for the controlled growth of thin layers of organic compounds if photo-, decomposition can be avoided or minimised during the laser interaction with the target. In this work we have studied the deposition process of 5CB (4-cyano-4'-pentylbiphenyl) liquid crystals films using different laser wavelengths: 193 nm (ArF), 248 nm (KrF), 308 nm (XeCl) and $10.6 \mu\text{m}$ (CO_2). Optical-UV and infrared absorption, optical microscopy and high performance liquid chromatography have been employed to analyse the structure and composition of the deposited material.

Films with optical properties similar to that of the starting material and no degradation were obtained by using the XeCl laser, although the morphology of the deposited films is found to be strongly dependent on the laser fluence and the deposition time. On the other hand deep UV and CO_2 lasers produce severe and partial decomposition of the deposited material.

The results are discussed in terms of the different nature of the laser-liquid crystal interaction process for the wavelengths considered.

G-IX.3 16:45-17:00

ABLATION OF SILVER AT 355 nm IN BACKGROUND GASES, T.N. Hansen, J. Schou, OFD, Riso National Laboratory, 4000 Roskilde, Denmark; Y.Q. Shen, NKT Research Center, Priorparken 878, 2605 Brøndby, Denmark and J.G. Lunney, Department of Physics, Trinity College, Dublin 2, Ireland

For pulsed laser deposition of many materials it is necessary to use a reactive background gas to facilitate the formation of the required phase. Thus there is a need to understand the dynamics of the transport of the ablation plasma through background gases and to characterize the plasma impinging on the growing film.

We have used a system of 15 ion Langmuir probes located in a circular array to measure the angular distribution and the time-of-flight spectra of the ions ablated from a silver target into inert and reactive atmospheres. The ion signals turn out to decrease strongly with the angle relative to the normal. In vacuum, the ion time-of-flight spectra has a single peak, but with an increasing pressure the ion signal gradually splits into two peaks. At oxygen pressures around 0.05 mbar the ion signal has a main peak due to ions transmitted through the gas with few or no collisions and a minor peak associated with plasma which is nearly thermalized by collisions. The probes were also used to monitor the variation of electron temperature in the deposition region normally applied.

SYMPOSIUM G

G-IX.4 17:00-17:15

UNUSUAL GROWTH OF PULSED LASER DEPOSITED BISMUTH FILMS ON Si(100), A. Dauscher, M.O. Boffoué, B. Lenoir, R. Martin-Lopez, N. Maloufi, H. Scherrer, Laboratoire de Physique des Matériaux, UMR 7556, Ecole des Mines, Parc de Saurupt, 54042 Nancy, France

The recent theoretical investigations on the use of quantum wells in thermoelectricity have shown that these two dimensional structures could have higher efficiency than three dimensional structures. Among materials, bismuth was proposed as being particularly interesting due to its peculiarities for thickness lower than 30 nm. This work was devoted to the study of the influence of both temperature and substrate nature on the growth process of pulsed laser deposited Bi films in order to control their structure and morphology.

Bi films have been grown by pulsed laser deposition (PLD) using the second harmonic mode of a Nd:YAG laser either onto glass or Si(100) substrates at various temperatures under high vacuum conditions.

Growth occurs in a completely different way on the two substrates at the first stages of the process as it has been evidenced by x-ray diffraction, atomic force microscopy, transmission electron microscopy, secondary ion mass spectroscopy and x-ray photoelectron spectroscopy. After a given thickness, the films tends to show similar structure, crystallite size and surface smoothness, whatever the substrate.

The peculiar type of Bi growth observed on Si(100) at the beginning of the process has to the best of our knowledge never been reported in the literature for any deposition method, until now. This study also contributes to the understanding of the basic phenomena occurring during the growth of pulsed laser deposited films.

G-IX.5 17:15-17:30

MnO THIN FILMS BY PULSED LASER DEPOSITION, W. Neubeck, C. Vettier, ESRF, BP 220, 38043 Grenoble Cedex, France and D. Givord, L. Ranno, Lab. Louis Néel, CNRS, BP 166, 38042 Grenoble Cedex, France

By using pulsed laser deposition under vacuum from Mn_2O_3 targets we were successful in growing epitaxial MnO thin films. The substrates used were sapphire (001) and MgO (111). Best results were achieved at a pressure of about 10^{-4} mbar and at substrate temperatures of around 700°C.

The films were characterised by using grazing incidence X-ray scattering as well as θ -2 θ Bragg scattering. Part of the characterisation was done with synchrotron radiation on the 4-circle diffractometer of ID20 at the ESRF/Grenoble. The films showed lattice parameters close to the bulk ones. The growth direction was found to be (111). The mosaicity is 0.1-0.2° depending on the film. By using AFM, images of the surface were taken. RBS measurements were used to check interdiffusion and film thickness. Typical film thicknesses were from 500Å up to 7000Å.

These films were used in non resonant magnetic X-ray scattering experiments at the ESRF, a third generation synchrotron facility. The obtained films evidenced antiferromagnetic character like in bulk crystals.

POSTER SESSION III

17:30-19:00

See programme of this poster session p. G-38 to p. G-45.

Friday June 19, 1998
Vendredi 19 juin 1998

Morning
Matin

SESSION X

Chairperson: I. Boyd, University College London, UK

- G-X.1** 8:30-9:00 - Invited - **INDUSTRIAL APPLICATIONS OF PULSED LASERS TO MATERIALS MICRO-PROCESSING**, M.C. Gower, Exitech Ltd, Hanborough Park, Long Hanborough, Oxford OX8 8LH, UK
During the past decade, excimer lasers have led the way in applying ablative material removal to micromachining applications in manufacturing industry. Recently short-pulse versions of more familiar industrial CO₂ and Nd:YAG lasers have also begun to be used for this application. The ability to drill ever smaller holes - down to ~1µm diameter, is an underpinning technology in many industries manufacturing hightech products. For example, precision microdrilling with excimer lasers is now routine when making some of the delicate medical probes which measure in-situ properties of blood in human arteries. The ~35µm diameter nozzle hole arrays in most of the ink jet printers currently sold in the world are now drilled by excimer lasers on production lines in Asia, Europe and the US. In 1988 Siemens first productionized the use of excimer lasers for drilling 80µm diameter electrical feed-through (via) holes in the multichip module (MCM) circuit boards that connect silicon chips together in high speed computers. In the interim period, trillions of vias have been drilled at yields of > 99.99% with lasers whose mean time between failures (MTBF) has been logged at >1,000 hours. Recently it has been found 'non-thermal' ablation can also be achieved with less-expensive pulsed CO₂ and Nd:YAG lasers. These are now used to drill vias at up to 200holes/sec in lower cost packages like flexible and printed circuit boards (FPC's and PCB's). We will review these and other applications of pulsed laser micro-processing in manufacturing industry.
- G-X.2** 9:00-9:15 **A NEW PROCESS TO MANUFACTURE THIN SiGe AND SiGaC EPITAXIAL FILMS ON SILICON BY ION IMPLANTATION AND EXCIMER LASER ANNEALING**, P. Boher and J.L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France; E. Fogarassy, Laboratoire PHASE, BP 20, 67037 Strasbourg Cedex, France
Silicon based high speed devices are intensively studied now. Based on SiGe alloy films, their are generally produced by high cost epitaxial techniques. In this paper, we explore a new way to realize epitaxial layers without need of UHV deposition techniques. SiGe and SiGeC films are realized on silicon using ion implantation coupled with excimer laser annealing. Flat concentration profiles of Ge and C are implanted inside monocrystalline silicon with a depth of the order of 150nm, using different implantation energies. Crystallization is obtained using a high power XeCl excimer laser and varying the energy density. New generation of lasers at SOPRA allow the obtention of 45J on one shot on the sample surface. In this conditions large areas can be treated with a good homogeneity. The crystallinity of the films before and after laser annealing is checked by different methods. X-ray diffraction provides the crystalline quality and the strains inside the layers. Spectroscopic ellipsometry gives the amorphous profile in the depth of the samples for low energy annealing and precise values of the optical transitions inside the epilayers. Channeling Rutherford backscattering will be used for final check of the monocrystalline character of the layers obtained by this method.
- G-X.3** 9:15-9:30 **POLYMER REPLICATION OF 3D MICRO STRUCTURES EMPLOYING A HIGHLY FLUORINE CONTAINING SEPARATION LAYER**, A. Braun, J. Meinhardt, K. Zimmer, B. Höbelbarth, F. Bigl, Institute of Surface Modification, Permoserstrasse 15, 04318 Leipzig, Germany
The combination of prototyping with a subsequent replication process has long been the choice for time efficient and economic production schemes. We adopted this method and developed a new technology for the fabrication of three dimensional micro structures based on excimer laser ablation of acrylic polymers and direct inverse replication. The individual dimensions measure 300 µm in width and up to 200 µm in height. The replicas are made of an acrylic monomer blend cured with UV-photons and electrons. In order to protect the master and to secure a safe and non-destructive separation of master and replica the master was coated homogeneously with a highly fluorine containing layer. This coating was applied employing an adjusted C₆F₁₄ plasma polymerization process resulting in an even ca. 5nm to ≥ 2µm thin anti-adhesion layer. In order to characterize the physical and chemical properties of the laser processed master and replicas we employed SEM, ESCA and optical profiling and will present the results in detail. The master's surface smoothness was measured to be in the low 10 nm range RMS-value and the surface's fluorine mass concentration could be raised up to 68.6 %. We have been observing a constant chemical composition at the replica's surface over a period of 50 replication cycles. The results demonstrate that the utilized anti-adhesion layer serves as a long living separation coating.
- G-X.4** 9:30-9:45 **MODELING OF NON-STATIONARY THERMAL VOLUME DESTRUCTION OF POLYMERS BY LASER LIGHT**, N. Arnold, D. Bäuerle, Angewandte Physik, J. Kepler University, Altenbergerstraße 69, 4040 Linz, Austria and N. Bityurin, Institute of Applied Physics RAS, Uljanov St., 603600 Nizhnii Novgorod, Russia
Modeling of laser ablation of polymers assumes either bond breaking by the photons or thermally activated processes. With polymers, bond breaking occurs within the bulk of the material. Thus, the surface temperature does not directly determine velocity of the moving boundary. We relate its position to the concentration of thermally broken bonds below the surface. Within the frame of this model we consider both the stationary and non-stationary ablation regimes, in particular near threshold behavior. Several differences with the surface thermal models are revealed (i) Despite thermal nature of the process, material removal starts very sharply as a junction of laser fluence or time (in a single pulse), while surface models reveal Arrhenius tails and gradual increase in the front velocity. (ii) The ablation velocity has a sharp peak just after the onset of ablation; after that the transition to the stationary ablation is very fast. This burst of ablation velocity may be responsible for the sound signal, sometimes taken as a definition of ablation threshold. (iii) Near threshold ablation may start significantly (some pulse lengths) after the peak of the temperature and/or the end of the pulse. This reflects the cumulative effect of the temperature onto the number of broken bonds. Modeling is applied to the description of experimental data on UV laser etching and ablation of PI.

SYMPOSIUM G

G-X.5 9:45-10:00

EVIDENCE FOR VOLUME BOILING DURING LASER ABLATION OF SINGLE CRYSTALLINE TARGETS, V. Craciun and D. Craciun, Laser Dept, NILPRP, Bucharest V, Romania

One of the first mechanisms suggested to be responsible for droplets emission during pulsed laser deposition (PLD) was the subsurface superheating effect. The model was quite popular until it was pointed out that its main assumptions, the fixed surface temperature and the corresponding boundary condition, are wrong. It has been further suggested that the subsurface boiling should be replaced with the concept of phase explosion, occurring when the temperature of the irradiated target reaches values close to 0.9 of the thermodynamic critical value. However, this does not explain the huge increase of droplet density onto the surface of PLD grown films observed when a laser wavelength which is poorly absorbed by the target was used for ablation. Moreover, the presence of circular-shaped, micron-deep cavities, observed after the ablation process by scanning electron microscopy investigations of Si and Ge monocrystalline targets when ablated by 1064 nm radiation is also difficult to explain using the phase explosion concept, but becomes easily understandable if the subsurface boiling mechanism is accepted.

10:00-10:30

BREAK

SESSION XI

Chairperson: R.D Vispute, CSR, University of Maryland, College Park, USA

G-XI.1 10:30-10:45

PLASMA IMMERSION ION IMPLANTATION FOR SHALLOW JUNCTIONS IN SILICON, L. Pinter, A.H. Abdulhadi, Zs. Makaro, N.Q. Khanh, M. Adam, I. Barsony, J. Poortmans* and G.J. Adriaenssen**, Res. Inst. for Techn. Phys. Mat. Sci. - MFA, P.B.Box 49, 1525 Budapest, Hungary, *IMEC, Kapeldreef 75, Leuven 3001, Belgium; **KU Celestijnenlaan 200D, Heverlee-Leuven 3001, Belgium

Formation of shallow junctions in Si is one of the main concerns in both ULSI and crystalline solar cell processing. Low cost Plasma Immersion Ion Implantation (PIII) offers the advantage of controllable doping at the expense of unintentional co-implantation of impurities due to the lack of mass separation. Besides, the contact between the plasma and the chamber walls may lead to serious metal contamination.

In this work the results of low voltage (<1keV) PIII for acceptor and donor doping will be reported on from plasmas of 1% B₂H₆-H₂ and 1%PH₃-H₂ gas mixtures, respectively. RBS was used to determine the thickness of the damaged layer formed in both processes. The sputtering rates of silicon were determined by the Xe marker technique. Saturation phenomena in the surface concentrations of the dopants can be attributed to the effect of simultaneous sputtering of the doped layers. The co-implanted hydrogen depth profile was measured by ERDA using 3555keV α -particles. The level of the co-implanted metal contamination was determined by RBS and DLTS techniques. Conventional annealing and RTA were applied for the activation of the dopants resulting in junction depths in the range of 0.1-0.2 μ m. The method will be applied in multicrystalline solar cells.

G-XI.2 10:45-11:00

TEMPERATURE DEPENDENCE OF EPITAXIAL GROWTH OF MAGNETORESISTIVE La_{0.7}Ca_{0.3}MnO₃ FILMS ON MgO(001), L. Ranno, A. Llobet, M.B. Hunt, J. Pierre, D. Givord, Laboratoire Louis Néel, Polygone CNRS, BP 166, 25 avenue des Martyrs, 38042 Grenoble Cedex 09, France

We have studied the growth of thin films of La_{0.7}Ca_{0.3}MnO₃ on MgO (001) single crystalline substrates. These films were synthesised using the pulse laser deposition method and two epitaxial modes have been evidenced as a function of substrate temperature, keeping the oxygen pressure constant (300 mtorr). Structural characterisations have been carried out using X-ray diffraction in θ -2 θ and grazing incidence geometries. These films undergo a ferromagnetic phase transition around 250 K and at the same temperature a metal-insulator transition takes place. Magnetoresistance (CMR) reaches -90% in a 5 T field at the transition temperature. The influence of the film structure on magneto-transport properties will be presented and low field MR at low temperature will be discussed in the framework of spin dependent tunneling models.

G-XI.3 11:00-11:15

GROWTH OF NON STOICHIOMETRIC OXIDE PHASES BY LASER ABLATION, A. Gutierrez-Llorente, M. Morcrette, A. Laurent, P. Barboux*, Groupe de Physique des Solides, Universités Paris VII et Paris VI, Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France; *Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Laser ablation is widely used for the growth of polycationic oxides. Moreover, due to the nonequilibrium nature of this process, and to the fact that the deposition can be carried out under a wide range of pressures (from 10⁻⁶ to 1 mbar) we can expect the formation of new oxide phases which cannot be easily grown in the bulk form. We have checked this idea by studying the growth of thin films from targets consisting of Ti⁴⁺-based perovskites (BaTiO₃ or Li_{0.33}La_{0.55}TiO₃) onto MgO (001) at high T. (6008C to 8008C) under oxygen pressure. Under high pressure, films of stoichiometric BaTiO₃ and Li_{0.33}La_{0.55}TiO₃ were obtained corresponding to an oxidation state Ti⁴⁺ like in the ceramic target. When deposited under high vacuum (<10⁻⁶ mbar), films are grown with the BaTiO_{2.7} and La_{0.66}TiO_{2.5} compositions. This means that Ti³⁺ are solely present in the deposited layers and that Li ions are not fixed in the last compound. Optical absorption measurements confirm the valence state of Ti in the film according to the O₂ pressure during the growth. In the bulk material such a phase has not been previously reported with such high vacancy level. The crystalline quality has been studied from rocking curves in X-ray diffraction or by RBS in channeling geometry. They indicate that the films are highly textured along (00l) and/or (hh0) direction. Epitaxial relationships have been also observed by asymmetrical X-ray diffraction, the in-plane orientation corresponding to the cube on cube growth. Moreover the Ti³⁺ films show interesting physical properties (high conductivities with a metal like behaviour), which permit the use of such films as a conducting oxide electrode in multilayers systems.

SYMPOSIUM G

G-XI.4 11:15-11:30

RELAXED LASER DEPOSITION OF SnO_2 THIN FILMS, N. Méquillet, D. Demange, M. Grivet and A. Chambaudet, Laboratoire de Microanalyses Nucléaires, 16 route de Gray, 25000 Besançon, France

This study presents the use of a Nd/YAG relaxed laser ($\lambda=1064\text{ nm}$, $\tau=150\text{ }\mu\text{s}$, $I<106\text{ W.cm}^{-2}$) in a reactive pulsed-laser deposition technique. In using the relatively low power density of this laser and a repetition rate of 10 Hz, SnO_2 thin films can be grown on silicon substrates by a tin target ablation in an O_2 atmosphere. The films are characterised ex-situ by Fourier transformed infrared spectroscopy, grazing incidence X-ray diffraction and scanning electron microscopy. Beforehand, some parameters governing the deposition, such as lens-target distance, pulse numbers, oxygen background pressure (0.4 mbar) and target-substrate distance must be optimised. Afterwards, post-annealed films deposited at room temperature are compared to films grown on heated substrates. The variation of the crystallinity of the films with an increasing temperature is reported. The films obtained with both methods are polycrystalline and exhibit a rutile structure of bulk SnO_2 . However, some optical and mechanical differences may appear.

G-XI.5 11:30-11:45

CHARACTERISTICS OF THE MICROSTRUCTURES OF ALUMINA-BASED REFRACTORY MATERIALS TREATED WITH CO_2 , ND-YAG AND DIODE LASERS, L. Bradley, L. Li, Manufacturing Division, Mechanical Engineering, F.H. Stott, Corrosion and Protection Centre, University of Manchester, Institute of Science and Technology (UMIST), PO Box 88, Manchester M60 1QD, UK

A study to improve the integrity and reliability of alumina-based refractory bricks, typically used to line furnaces and incinerators, is being conducted. Different origins and types of fuel will impose different environmental conditions on the materials of construction. Two properties have a great effect on the chemical reactions which take place between refractory lining and slag or effluents. The first, chemical compatibility, is of primary importance, however, since no single refractory is suitable for all the corrosive environments with which it may come into contact, the second most important property is penetration resistance. This study involves an investigation of the optimum laser processing parameters that will produce a zone of pore-free, crater-free and crack-free material at the refractory surface. This treated zone can reduce/eliminate the ingress of slags and gases, thus providing a reduced area for attack by corrosive species. Treating the refractory materials with CO_2 , diode and Nd-YAG lasers produces a surface zone of varying thickness and with different microstructural characteristics. The performance of the treated refractories has been assessed in laboratory-simulated waste incineration environments and compared with that of the untreated bricks.

G-XI.6 11:45-12:00

IN-SITU MEASUREMENT OF LASER IRRADIATED ZINC SULPHIDE FILMS, J.D. Hoyland, D. Sands, P.H. Key, Physics Department, University of Hull, Cottingham Road, Hull HU6 7RX, UK

The surface temperature of thin film zinc sulphide on silicon during and after pulsed excimer laser irradiation, has been measured by the use of time resolved reflectivity. The aim of this work is to verify earlier studies of laser ablation of ZnS in which ablation rate was conjectured to be directly related to surface temperature, and that surface melting is not a significant mechanism in the ablation process.

A computer simulation was developed to model the reflectivity changes induced by pulsed laser irradiation. The temperature dependant optical properties of ZnS were also verified by us experimentally. The samples were irradiated, in an argon ambient, by a 25ns pulse from a XeCl excimer laser (308nm), over a range of fluences from 89 mJ.cm^{-2} to 201 mJ.cm^{-2} . Using a cw diode laser, the reflectivity was monitored during and after irradiation. From the model it was then possible to determine the temperature profile in the sample. The results showed that the modelled surface temperature is accurate to within 50°C up to and at the ablation threshold. At significantly greater fluences, the reflectivity signal becomes complicated by effects other than surface temperature, caused by the optical properties of the ablated material. However the results suggest that melting does not play a significant role in the ablation process. In addition the results suggest ablation takes place within the first few nanoseconds after the end of the pulse.

12:00-14:00

LUNCH

Friday June 19, 1998
Vendredi 19 juin 1998

Afternoon
Après-midi

SESSION XII

Chairperson: C. Boulmer-Leborgne, GREMI, Université d'Orléans, Orléans, France

G-XII.1 14:00-14:15

STABILITY, ENHANCEMENT OF ELASTIC PROPERTIES AND STRUCTURE OF MULTILAYERED AMORPHOUS CARBON FILMS, S. Logothetidis, M. Gioti, C. Charitidis, P. Patsalas, J. Arvanitidis and J. Stoemenos, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

The growth of sputtered amorphous carbon (a-C) films in layer structure with alternative (negative/positive) substrate bias voltage V_b , was applied to control their intrinsic stress level and stability. The main benefit of the process was the development of stable and rich in sp^3 sites thick films proving their usefulness for many practical applications. In order to investigate the structure, the mechanisms of film stability and the modifications induced by ion bombardment either during deposition or postgrowth we performed in-situ Spectroscopic Ellipsometry (SE), Stress, X-rays Diffraction (XRD) and Reflectivity (XRR), Transmission Electron Microscopy (XTEM), Nanoindentation and Raman measurements. It was found a stress relief to occur in films depending on the sequence of layers and their modulation period. Despite the film stability an improvement in their hardness and elastic modulus values was achieved that are above all, so far, reported ones for the sputtered a-C films. Detailed analysis of SE data provide information about the modifications in the composition (sp^3 , sp^2 bonds and voids) and thickness of the underlying layer when deposited a layer with $V_b < 0$ (ion bombardment during growth). From XRR the layers densities and thickness are obtained and compared with those from XTEM. The latter technique provides details about the layered structure of the as grown and the postgrown bombarded films with ion energies above 1keV. Finally, the results are discussed in view of the carbon phases amorphous and microcrystalline detected and identified in the as grown and postgrown bombarded films by XRD, XTEM and Raman.

G-XII.2 14:15-14:30

XeF EXCIMER LASER ABLATION OF METALLIC TARGETS PROBED BY ENERGY-SELECTIVE TIME OF FLIGHT MASS SPECTROMETRY, S. Amoroso*, V. Berardi**, R. Bruzzese**, R. Velotta**, N. Spinelli*, X. Wang**, Istituto Nazionale per la Fisica della Materia and *D.I.F.A. - Università della Basilicata, via della Tecnica 3, 85100 Potenza, Italy; **Dipartimento di Scienze Fisiche, Complesso Universitario di Monte S. Angelo, Via Cinzia, 80126 Napoli, Italy

We report on the diagnostics of the plasma produced in XeF laser ablation of metallic targets (Al and Cu). By using an energy-selective time of flight mass spectrometer, we measured the kinetic energy distribution (KED) of Al^+ and Cu^+ ions at various laser fluences. The experimental (KED show a double-peak structure. The first peak is located at low kinetic energy (~ 1 eV) and is related to a thermoionic component, the second one is strongly dependent on laser fluence and is due to energetic ions emitted from the laser produced plasma. In laser ablation of Cu we observed only the thermal component up to a laser fluence lower than ~ 2.6 Jcm $^{-2}$, whereas in Al the high kinetic component is always present. Since copper and aluminum have similar thermo-physical properties, but different ionisation potentials and electronic configurations, the results can be analysed in terms of the basic mechanisms involved in laser-vapour interaction and plume ionisation.

G-XII.3 14:30-14:45

ON THE ROLE OF AMBIANT OXYGEN IN FORMATION OF LEAD TITANATE PLD THIN FILMS, N. Chaoui, E. Millon, J.F. Muller, Laboratoire de Spectrométrie de Masse et de Chimie Laser, IPEM, Université de Metz, 1 bd Arago, 57078 Metz cedex 3, France and P. Ecker, W. Bieck, H.N. Migeon, Centre de Recherche Public, Laboratoire d'Analyse des Matériaux, 162 avenue de la Faïencerie, 1511 Luxembourg, Luxembourg
Among various ferroelectrics, lead titanate $PbTiO_3$ (PTO) is commonly used because of its superior ferroelectric and piezoelectric properties. By PLD, PTO films are obtained under high substrate temperature and rather large oxygen pressure. Poor informations are known about the origin (target or ambient gas) and the role of oxygen in PTO films formation. ^{18}O tracing experiments [1,2] constitute a powerful mean to solve this question. Our PTO films have been deposited on polycrystalline platinum substrate at a temperature of 550°C and under 3.10^{-4} mbar ambient ^{18}O (97% pure) pressure. The fluence and repetition rate of the laser (frequency quadrupled Nd-YAG, 266 nm, 6 ns) were changed in a range of 3-10 J/cm 2 and 2-10 Hz respectively. X-ray diffraction patterns of the obtained films indicate a perovskite structure with a random crystallographic orientation. SEM micrographies show two-dimensional grain structure (mean size = 200 nm). Each obtained film has been analysed by Dynamic SIMS in order to determine the concentration profile of ^{16}O (target) and ^{18}O (gas). The effect of the fluence, the repetition rate and the cooling on oxygen incorporation in the film is discussed and practical conclusions for laser deposition are proposed.

1 M.R. Predtechensky, A.N. Smal, B.A. Kolesov, V.P. Ivanov, Appl. Supercond., 1, 2005, 1993

2 R. Gomez- San Roman, R. Perez Casero, C. Marechal, J.P. Enard, J. Perrière, J. Appl. Phys., 80, 1787, 1996

G-XII.4 14:45-15:00

DEPOSITION OF THIN FILMS OF METALS ON CARBIDES AND SILICATE MICRO-AGGREGATES AND APPLICATIONS, M. Grosmann, F. Kintz, A. Akhmin, EPF, ENSPS-ULP, 67000 Strasbourg, France and V.G. Syrkin, GNICTEOS, Ac. Sc., Moscow, Russia

Thin conducting metallic films (Iron, Cobalt, Nickel ; Gold, Rhodium, Vanadium) have been deposited by CVD (Chemical Vapor Deposition) and RCPAVD (Reactive Chemical and Photon Assisted Chemical Vapor Deposition) on different substrates:

- thin optical thin films for photonics applications

- small aggregates of carbides and organo-silicates for industrial (biochemical and thermal) applications.

The films were deposited at relatively low temperatures by decomposition of carbonyl metals. Characterization of the substrates, films and aggregates at the different steps of preparation have been performed by different techniques (electron microscopy, micro- holography etc ...)

The results offer possibility of design of new components. A software based on Z-MAX is presented to optimize these processes.

SYMPOSIUM G

G-XII.5 15:00-15:15

STUDY OF METALLIC THIN FILM GROWTH BY PLASMA SPUTTER DEPOSITION, A.L. Thomann, J.P. Rozenbaum, P. Brault, GREMI, Université d'Orléans, Faculté des Sciences, B.P. 6759, 45067 Orléans cedex 2, France; C. Andreazza-Vignolle, P. Andreazza, H. Estrade-Szwarckopf, and. B. Rousseau, CRMD, 1B rue de la Férollerie, 45071 Orléans cedex 2, France

We are studying the deposition of metallic thin films exhibiting catalytic properties by plasma sputter deposition. Our aim is to show that this method may be a relevant way to synthesize such catalytic objects, compared to techniques used at the present time (liquide phase or UHV deposition methods). In this method, the atomic metal source is a negatively biased wire submitted to the sputtering action of Ar ions created in a HF plasma. The metal deposition rate depends on the sputtering efficiency which is governed by the argon pressure (number of Ar ions) and the wire bias voltage (Ar ion energy). Since the substrate surface is submitted to the Ar plasma, the deposition process is also dependent on the gas pressure. The argon plasma is analyzed by means of electric measurements (Langmuir probe) which allow to estimate the Ar^+ flux near the wire (sputtering process) and at the substrate location (deposition process). The deposit morphology is examined by transmission electron microscopy, scanning tunneling microscopy and grazing incidence small angle X-ray scattering. First results have shown that the growth mode of palladium films on silicium native oxide is Volmer-Weber, involving the formation of small aggregates (morphology required for catalysts). This work has evidenced differences in scale laws governing the growth compared to vacuum deposited films which is attributed to the plasma action on the substrate surface during the deposition process.

G-XII.6 15:15-15:30

PULSED LASER ABLATION AND DEPOSITION OF $\text{ZnS}_x\text{Se}_{1-x}$ THIN FILMS ON QUARTZ: ENERGY GAP MODULATION AND EFFECT OF THE DISORDER ON THE ABSORPTION COEFFICIENT M. Ambrico, C. Spezzacatena, D. Smaldone I.M.S.-C.N.R. via S.Loja-Zona Industriale, 85050 Tito Scalo (PZ), Italy, V.Capozzi, G.Perna, Dip. Fisica and Unita' INFM Università di Bari via Amendola 173, 70100 Bari, Italy

The choice of depositing high quality ZnSSe thin films was suggested by the necessity of creating VIS/UV optical windows and to obtain the band gap modulation in this range. Despite their interesting optical properties, thin films of these alloys show a very poor crystallinity no matter what is the deposition technique used for their production.

In this work we report results on the gap modulation in $\text{ZnS}_x\text{Se}_{1-x}$ thin film which have been deposited by Pulsed Laser Ablation on quartz.

Room temperature transmittance and reflectance measurements have been carried out in order to obtain the experimental trend of the absorption coefficient and energy gap as a function of the sulfur concentration. A new calculation of the theoretical absorption coefficient is presented according to new models which take into account the effect of the disorder in the trend of the absorption coefficient below the energy gap and particularly in the absorption tail zone.

END OF SYMPOSIUM G

SYMPOSIUM G
SYMPOSIUM G
POSTER SESSIONS

Tuesday June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-midi

Poster Session I
17:30-19:00

- G-I/P1** **THE PRODUCTION OF THE NEW CUBIC FeN PHASE BY REACTIVE MAGNETRON SPUTTERING**, L. Rissanen, P. Schaaf, M. Neubauer, K.-P. Lieb Universität Göttingen, II. Physikalisches Institut, Bunsenstrasse 7/9, 37073 Göttingen, Germany; J. Keinonen, T. Sajavaara, Accelerator Laboratory, University of Helsinki, P.O.Box 43, 00014 Helsinki, Finland
FeN films with nearly 50 at.% nitrogen content were prepared by reactive magnetron sputtering [1,2,3]. The influence of preparation parameters (gas flows, substrate temperature and bias, RF power) on film growing conditions are investigated. The phase structure and its stability when heating in different atmospheres were characterized by XRD, TEM, RBS, RNRA, CEMS, and TOF-ERDA. The XRD and TEM diffraction patterns exhibit two fcc phases (g"- and g'''-FeN). The g"-phase has a ZnS-type structure and g'''-phase a NaCl-type structure [4]. The analyses of the CEMS measurements are discussed with respect to the nitrogen content.
[1] M. Niederdrenk et al., J. Alloys and Compounds 237 (1996) 81
[2] P. Schaaf et al., Hyperfine Interactions 99 (1995) 566
[3] L. Rissanen et al., "ICAME-95" Conference Proceedings Vol.50, ed.I. Ortalli (SIF, Bologna, 1996) 595
[4] H. Nakagawa et al., Hyperfine Interaction 69 (1991) 455.
- G-I/P2** **LASER-NITRIDING OF IRON: EFFECTS OF THE SPATIAL INTENSITY DISTRIBUTION**, F. Landry, P. Schaaf, M. Neubauer, K.-P. Lieb; Universität Göttingen, Zweites Physikalisches Institut, Bunsenstrasse 7/9, 37073 Göttingen, Germany
The effect of the nitrogen take-up upon irradiation of iron or steel with excimer laser pulses in air or nitrogen atmosphere is well established [1,2]. Resonant Nuclear Reaction Analysis (RNRA) utilising the reaction $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ and surface profilometry have already been used to investigate the characteristics of the nitrogen distribution and the surface topology for irradiation with the focused raw beam of the laser [3]. The additional usage of a beam homogeniser leads to substantially different results. Among these are a strongly reduced piston-effect, a more homogeneous lateral nitrogen distribution and depth profile with a saturation concentration of 10 at.% in a depth of 300 nm as compared to 3-4 at.% for irradiation with the raw beam. We will discuss these differences with respect to pulse number, energy density and background pressure, leading to a further insight into the influence of the different competing processes during the laser nitriding of iron and steel.
[1] C. Illgner, K.-P. Lieb, P. Schaaf, K. Mann, H. Köster and G. Marowsky, Appl. Phys. A 62, 231 (1996)
[2] C. Illgner, P. Schaaf, K.-P. Lieb, E. Schubert, R. Queitsch and H. W. Bergmann, Appl. Phys. A 61, 1 (1995)
[3] C. Illgner, P. Schaaf, K.-P. Lieb, R. Queitsch and J. Barnickel, J. Appl. Phys. (1998), in press.
- G-I/P3** **DRY ETCHING OF Cu WITH Cl₂ STIMULATED BY SYNCHROTRON RADIATION**, H. Raaf and N. Schwentner, Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
Light induced dry etching of polycrystalline Cu plates with Cl₂ using Synchrotron Radiation in the range of 50 nm to 300 nm has been investigated with respect to selectivity, spatial resolution, anisotropy, product distribution and efficiency of the photochemical processes. By reproduction of Ni-masks we observed the growth of CuCl₂-films in the micrometer range with a submicrometer spatial resolution. Selective and nonselective reactions could be separated via the Cl₂ partial pressure. The nonselective reactions originate from a gasphase excitation of Cl₂, while the selective ones are due to an excitation of adsorbed molecules. AES- and XPS-depth profiling studies indicate for the selective reaction a chain reaction of the adsorbate with Cu which reached the surface by diffusion. The swelling behaviour results from the lower density of the CuCl_x-films.
- G-I/P4** **PULSED LASER DEPOSITION FROM SOLID AND MOLTEN METALS**, T. Szörényi, Z. Kantor*, Z. Toth, P. Heszler and L. Gombos*, Research Group on Laser Physics of the Hungarian Academy of Sciences, *Department of Optics and Quantum Electronics, Jozsef Attila University, POB 406, Szeged 6701, Hungary
Particulate formation is a major problem in Pulsed Laser Deposition (PLD). It has been claimed by several authors that ablating liquid targets, i.e. using self-reproducing smooth surfaces allows for particulate-free film deposition. However, in all recent liquid-target PLD experiments resulting in particulate-free films the deposited material was different from the target, and the substrate temperature was definitely higher than the melting point of the target material, rendering the survival of possible particulates landing at the hot surface impossible.
In this paper we aim at deciding whether particulate formation can generally be avoided by using liquid targets, or only particulate deposition was suppressed by choosing appropriate experimental circumstances in the reported experiments. We deposited indium films from solid and liquid In targets in vacuum (i.e. we deposited the same material as we ablated). The substrates were held near room-temperature in order to collect and preserve the droplets if formed. Ablating molten targets of different temperature, the particulate number density decreased by orders of magnitude as compared to the solid-target case. However, particulate formation could not be totally eliminated.
- G-I/P5** **ON THE DYNAMICS OF LASER - INDUCED ETCHING OF TUNGSTEN - SiO₂- COMPOSITES**, K. Piglmayer, H. Schieche, Angewandte Physik, Johannes-Kepler-Universität Linz, 4040 Linz, Austria
CW laser induced heating of W- SiO₂ - layer composites in a WF₆ -atmosphere results in a locally well defined removal of W from the SiO₂ substrate. High resolution etching of the processing area is possible due to the nonlinearity of the kinetics.
The process is simulated using a three-dimensional numerical model, including the time dependent evolution of the etch front and the corresponding temperature distribution. All the temperature dependent material parameters and time dependent absorption characteristics are taken into account.
The results obtained from the model are compared with experimental investigations.

- G-I/P6** INFRARED ABSORPTION DIAGNOSIS OF ORGANOSILICON/OXYGEN PLASMA IN A MICROWAVE MULTIPOLAR DECR PLASMA, P. Raynaud, T. Amilis, Y. Segui, Laboratoire de Génie Electrique, CNRS, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex, France
Organosilicon/oxygen plasma are used to realize SiOx films in view of obtaining properties on different substrates such as : insulating films, oxygen barrier films, hard coatings...The standard diagnoses of the plasma phase (U.V.- visible emission spectrometry, Langmuir probe measurements) do not give a direct access to the initial molecular structure as well as to the structure of the species resulting from their dissociation. Fourier Transform Infra-Red (FTIR) spectrometry allows the detection of bonds in these species. In this way, four organosilicon groups [HMDSO, TEOS, TMS and TMOS] in mixture with oxygen, have been analyzed using F.T.I.R. absorption spectrometry in a MMP-DECR reactor. The dissociation of each organosilicon group is analyzed as a function of the power (50 to 400 W) and as a function of the mixture with oxygen. The correlations are obtained through measurements by mass spectrometry. It appears that the molecules are totally dissociated above 100 watts. Thereafter, one finds stable species such as CH₄, C₂H₂, C₂H₄, OCH₃, CO, CO₂ and R-SiH. Each group exhibits its very own characteristics depending on its basic structure. The IR measurements confirm the extreme effectiveness of DECR plasma in the molecular dissociation. It seems that the precursors of deposits, are the atomic species which interact with the substrate surface. More generally, the I.R. spectrometry will permit to have an access to the rotational temperature of the molecules as well as to the quantitative measurements of certain species such as CH₄. The entire set of diagnoses (IR, mass spectrometry, U.V. visible emission spectrometry and Langmuir probe) should permit a better understanding of the mechanisms involved in the plasma phase of these complex molecules.
- G-I/P7** MODELLING OF LASER PRODUCED PLASMA AND TIME OF FLIGHT EXPERIMENTS IN UV LASER ABLATION OF ALUMINUM TARGETS, S. Amoroso, Istituto Nazionale per la Fisica della Materia and D.I.F.A., Università della Basilicata, via della Tecnica 3, 85100 Potenza, Italy
A theoretical model and an experimental analysis of the plasma produced in UV laser ablation of metallic targets is reported. We have measured time-of-flight (TOF) distributions of positive ions, ion maximum kinetic energies and total ion and electron yield. All the laser plasma parameters increase with the laser fluence until a plateau is reached at high fluence. This behaviour is ascribed to photon absorption and vapour ionisation mechanisms active in the laser ablation process at UV wavelengths. A model of laser-solid-plasma interaction taking into account vapour ionisation and absorption mechanisms and laser induced plasma kinetics was developed. The model shows that the plasma parameters, which are increasing function of the fluence at moderate laser intensities, approach a plateau regime at high laser fluences. The good agreement of the model with the experimental behaviour confirms that laser-plasma interaction processes and plasma kinetics are of great importance in nanosecond laser ablation of metallic targets for power densities of the order of $\sim 10^9 \text{ Wcm}^{-2}$.
- G-I/P8** INVESTIGATION OF LASER PLASMA FOR SOLID ELEMENT COMPOSITION MICROANALYSIS, V. Detalle, J.-L. Lacour, P. Mauchien, A. Semerok, CEA Saclay, DPE/SPCP/LSLA, 91191 Gif sur Yvette Cédex France
Laser ablation optical emission spectroscopy for element composition microanalysis of solid samples was applied in our work. This method permitted to obtain a quantitative element concentration mapping with spatial resolution less than 10 μm . The analytical characteristics (LTE existence, excitation temperature, plasma plume expansion, duration of analytical spectral lines) of the plasma formed at atmospheric pressure were under investigation. The experiments were performed with the fourth harmonic of Nd-YAG laser beam (266 nm, 4 ns duration) focused to 10 μm spot into a solid target. Iron was chosen as an analytical element for plasma parameters measurements because of its very rich spectrum with optical transitions from the excited levels in energy range from 27395 cm^{-1} to 52655 cm^{-1} . The Einstein coefficients of iron are well known with sufficient precision. For avoiding the self absorption effect, we have used borax sample with low iron concentration (0.2%). Spectral zone from 370.5nm to 377.0 nm was chosen for our experiments. The Local Thermodynamical Equilibrium was tested by the Boltzmann plot method for different zone of plasma during its temporal evolution. The experimental results of plasma plume expansion, analytical lines temporal changes, LTE and excitation temperature spatial/temporal distribution are presented and discussed.
- G-I/P9** LASER ABLATION EFFICIENCY OF METAL SAMPLES WITH UV LASER NANOSECONDS PULSES, B. Sallé, C. Chaléard, V. Detalle, J.L. Lacour, P. Mauchien, C. Nouvellon, A. Semerok, CEA Saclay, DPE/SPCP/LSLA, 91191 Gif sur Yvette Cédex France
High intensity laser pulse interaction with a solid sample leads to the formation of a crater resulting from matter ejection. As the laser/ surface interaction depends on physical properties of a solid, environmental conditions and laser parameters (wavelength, pulse duration, energy, laser beam diameter), the characterisation of crater is an interesting method to understand the physics of the ablation process. In this work, the crater created on the surface sample was characterised by its depth, diameter and volume determined by a phase-stepping profilometer with lateral resolution $\sim 0.5 \mu\text{m}$ and depth resolution $\sim 0.01 \mu\text{m}$. The experiments were performed with Excimer (248 nm wavelength, 20 ns pulse duration) and Nd-YAG (266 nm wavelength, 4 ns pulse duration) lasers, in air at atmospheric pressure on different metal samples (Mo, Fe, Mn, Cu, Al, Zn, Pb and Sn). Laser pulse intensities varied from 0.5 GW/cm^2 to 50 GW/cm^2 . The influence of laser pulse number, properties of matter and laser pulse energy on the crater sizes was investigated. The experimental results obtained are presented and compared with the existing models of laser ablation.
- G-I/P10** STOICHIOMETRIC STUDY OF ABLATION PROCESS FOR MULTIELEMENTAL ANALYSIS BY OPTICAL EMISSION SPECTROSCOPY ON LASER PRODUCED PLASMA, C. Nouvellon, C. Chaléard, J.L. Lacour, P. Mauchien, Analytical Laser Spectroscopy Group, CEA Saclay 91191 Gif sur Yvette Cédex, France
For quantitative multielemental analysis by Optical Emission Spectroscopy on Laser Produced Plasma (SEO-LPP), the plasma composition must be representative of the sample composition. Stoichiometry of ablation process is often suggested and may vary with laser energy conditions. Our work deals with verification of stoichiometric behaviour for two values of laser energy. For this purpose, we study the vaporisation-atomisation rates of different elements in the sample, at different delays after laser pulse. The study concerns two kinds of samples, an alloy with minor elements (few % of Cu, Zn, and Mg in aluminium) and a binary alloy (brasses: Cu and Zn). Elements are chosen in order to compare results regarding melting points and atomic masses. For both values of energy, stoichiometric ablation process is verified for sample with minor elements. We don't have the same results for binary samples. Calibration curves prove that we have a non understood behaviour for copper. Localisation of the species in the sample can be seen using a CCD camera and interference filters to complete the study.
- G-I/P11** EXPERIMENTAL INVESTIGATIONS OF LASER ABLATION EFFICIENCY OF PURE METALS WITH FEMTO, PICO AND NANOSECOND PULSES, A. Semerok, C. Chaléard, V. Detalle, J.-L. Lacour, P. Mauchien, P. Meynadier*, C. Nouvellon, B. Sallé, P. Palianov**, M. Perdrix*, G. Petite**, DPE/SPCP/LSLA, *DSM/DRE-CAM/SPAM, **DSM/DRECAM/SRSIM, CEA Saclay, 91191 Gif sur Yvette Cédex, France
Three different lasers were used for laser ablation experiments with pure Al, Cu, Mo, Fe, Pb and Ni samples: 1) Nd-YAG laser with a 4 ns pulse duration being emitted on the second and the fourth harmonics in the 6 - 126 μJ energy range; 2) Nd-YAG laser with output energy of 70 mJ per pulse at 1064 nm with a 25 ps pulse duration. The fundamental frequency was doubled and quadrupled by two KDP crystals; 3) Ti-sapphire laser with a 150 fs pulse duration, yielding energy up to 60 μJ on 400 nm. The laser beams were focused onto the spots of around 10 μm diameters (Nd-YAG lasers) and of 30 - 50 μm diameters (Ti-sapphire laser). The craters formed in samples were examined by means of a phase-stepping profilometer with lateral resolution $\sim 0.5 \mu\text{m}$ and depth resolution $\sim 0.01 \mu\text{m}$. The best ablation efficiency was obtained with a fs laser. The ablation efficiency was found to be higher for a ns pulse than for a ps pulse for the same wavelength. Various laser ablation models and the obtained experimental results are discussed.

- G-I/P12** **UV INTENSITY MEASUREMENT FOR 308 NM EXCIMER LAMPS USING CHEMICAL ACTINOMETER, J.-Y. Zhang and I.W. Boyd, Dept. of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK; H. Esrom, Fachhochschule für Technik Mannheim, Institute of Technology Mannheim, 68163 Mannheim, Germany**
Chemical actinometry has been employed in photochemistry as a relatively simple and accurate method for absolute radiation measurement. It possesses many advantages compared with physical methods used for this purpose, in that it is basically very simple and requires no specialised equipment. Furthermore it is less prone to systematic error, gives more reproducible results and does not demand any recalibration. The ferrioxalate actinometer is one of the classical systems commonly used as an actinometric standard. Though this has universal applicability, it has some disadvantages in its complexity and is rather time consuming in the associated analytical procedures required. Therefore, a large number of alternative actinometers have been proposed in recent years. In this paper, photolysis of 3,4-dimethoxynitrobenzene in alkaline media has been used for the determination of the ultraviolet (UV) intensity output of a XeCl* excimer lamp providing intense narrow band radiation at $\lambda = 308$ nm. The intensity measurement is based on UV spectral absorption measurement of the 2-methoxy-5-nitrophenolate anion formation from photolysis of 3,4-dimethoxynitrobenzene. This actinometer is shown to be particularly convenient for photolysis studies and measurements of UV intensities at wavelengths between 200-450 nm. A photokinetic model is presented for the reaction which can also be more generally applicable to any two component photochemical system. The UV intensity output and the efficiency of the lamps was investigated at different electrical powers and different geometrical distances.
- G-I/P13** **GROWTH OF TANTALUM PENTOXIDE FILM BY PULSED LASER DEPOSITION, J.-Y. Zhang and I.W. Boyd, Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK**
Tantalum pentoxide film has rapidly evolved as an important material for research in microelectronics. It is a promising candidate as a capacitor insulator in high density dynamic memories (DRAMs) due to its high dielectric constant (about 25) and its chemical and thermal stability, with the promise of compatibility with standard microelectronic processing. The pulsed laser deposition (PLD) technique has already been applied successfully to grow a variety of high quality films, such as high-Tc superconductors, ferroelectrics and dielectric materials. In this paper we describe the growth of thin films of Ta₂O₅ by PLD on quartz and silicon substrates by 532 nm (Nd:YAG) in various O₂ gas environments. The influence of the deposition parameters, such as oxygen pressure, substrate temperature and annealing, on the properties of the grown films, has been studied. The refractive index of the films increases with an increase in the pressure of O₂. X-ray diffraction measurements show that the as-deposited films are amorphous at temperatures below 500°C and possess orthorhombic (β -Ta₂O₅) crystal structure at temperatures above 600°C. The optical properties determined by UV spectrophotometer also strongly depend on the deposition parameters. The dependence of the film properties on subsequent annealing steps has also been investigated by FTIR (Fourier transform infrared spectroscopy). At O₂ pressure above 0.15 mbar, the refractive index of the films is about 2.1 which is close to the value of the bulk Ta₂O₅ of 2.2. The optical transmittance around 85% in the visible region of the spectrum can be obtained at oxygen pressure of 0.2 mbar. These results indicate that PLD can be an advantageous deposition technique for dielectric and optical films.
- G-I/P14** **NONLINEAR OPTICAL PROPERTIES OF METALLIC SURFACES F.P. Lohner and A.A. Villaeys, Institut de Physique et Chimie des Matériaux de Strasbourg / GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France**
Recent experimental work on nonlinear optical properties of metallic surfaces exhibit rotational and azimuthal anisotropies of the second harmonic intensity. In the present work, we analyze theoretically these results in order to get a simple characterization of the in-plane and out-plane nonlinear optical response of the surface. The theoretical description is based on an analytically tractable model deduced from a band model. The evaluation involves the determination of the surface states, of the corresponding interaction matrix elements and of the subsequent polarization induced by the exciting laser beam. In the particular case of Aluminum, these evaluations are made possible by the introduction of the nearly free electron model, valid for simple metals. For the Al (111) surface, the spectrum, as well as the rotational polarization anisotropy and azimuthal anisotropy have been determined and show a good agreement with experimental data. Of particular interest is the simple evaluation from the experimental anisotropy curves of the ratio between the normal component over the sum of the corresponding parallel components to the surface of the second-order optical susceptibility. This description opens the way to a more detailed microscopic description of adsorbed systems on metallic surfaces.
- G-I/P15** **THE INFLUENCE OF CARBON ON LASER-NITRIDING OF STEEL, P. Schaaf, F. Landry, M. Neubauer, Universität Göttingen, Zweites Physikalisches Institut, Bunsenstrasse 7/9, 37073 Göttingen, Germany**
It is well known that the irradiation of pure iron and steel with pulses of an excimer laser leads to a large dissolution of nitrogen into the irradiated surface [1]. In the present study the nitriding of plain carbon steels with increasing carbon contents (Armco, C15, C45, C80, C105) is investigated. Phase analysis is performed via Conversion Electron Mössbauer Spectroscopy (CEMS). The phases austenite (γ -Fe(C,N)), martensite (α') and ϵ -nitride (carbonitride) are identified in the laser-nitrided surfaces. The nitrogen depth profiles are determined by Resonant Nuclear Reaction Analysis (RNRA) utilising the reaction $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$. In all cases 15-30 at.% nitrogen are found at the surface decreasing with depth. The hardness of the nitrided surfaces is determined by the nanoindentation method. For all samples a clear enhancement of the surface hardness is found. The increase in hardness due to the laser treatment increases with the carbon content with a maximum at C80. Also the hardening depth shows this behaviour with a maximum of almost 2 μm for C80. The maximum in hardness is correlated with a maximum in the ϵ -Fe_{1-x}N content as revealed by CEMS phase analysis and a maximum in nitrogen uptake as determined by RNRA. The amount of the γ -Fe(C,N) phase was found to be higher for the carbon steels as compared to pure iron.
[1] C. Illgner, P. Schaaf, K.-P. Lieb, R. Queitsch and J. Barnickel, J. Appl. Phys. (1998), in press and referenced therein
- G-I/P16** **PATTERNED SURFACES IN P-TYPE SILICON BY PHOTODEFINED ETCHING, M.C. Martins, R.M. Gamboa, J.M. Alves, J.M. Serra, A.M. Vallêra, Dep. Fisica, Univ. de Lisboa, Campo Grande, 1700 Lisboa, Portugal**
In this article a simple technique for photodefined etching on p-type silicon is presented. The technique thus studied involves wet photoselective corrosion of silicon by an aqueous solution of a strong oxidising agent (Bromine). The etching process can be largely inhibited by light, allowing the shaping of photodefined 3-D structures on the surface of p-type silicon samples. These structures are not dependent on crystalline orientation which is an important advantage in polycrystalline silicon texturing. Furthermore, the process is lead through at open circuit conditions, which means that electrical contacts are not required. The fundamentals behind the process, involving electrochemistry of semiconductors, are presented along with a discussion of the process parameters. Efforts are being made to find the optimal conditions for maximum contrast and lateral resolution. As an example we present a practical application to the texturization of polycrystalline silicon for solar cells.
- G-I/P17** **OPTICAL PROPERTIES OF CdS AND CdSe LASER ABLATED THIN FILMS ON QUARTZ V. Capozzi, G. Perna, Dipartimento di Fisica e Unita, INFN dell'Università di Bari via Amendola 173, 70100 Bari, Italy; M. Ambrico, C. Spezzacatena, D. Smaldone, I.M.S.-C.N.R., C.da S.Loja-Zona Industriale, 85050 Tito Scalo (PZ), Italy; A.C. Felici, T. Papa, M. Piacentini Dip.di Energetica, Università La Sapienza Via A. Scarpa 14, 00161 Roma, Italy**
In recent years, CdS and CdSe have become very important for the production of several electronic and optoelectronic devices. In this work, we discuss the optical features of CdS and CdSe thin films which have been deposited in optimized conditions on quartz substrates. Transmittance and reflectivity measurements have been carried out as a function of temperature, in order to investigate the electron-phonon interaction and the energy gap shrinkage due to impurity disorder. The experimental results have then been fitted to what described in classical and new phenomenological models. The room temperature optical absorption of the CdSe film has been studied using the photoacoustic technique with a microphone detection. A comparison of the transmission spectrum of the same sample has allowed an estimation of the thermal diffusivity of the film.

- G-I/P18** TiN GROWTH ON Si(100) BY PULSED LASER DEPOSITION USING HOMOGENIZED KrF EXCIMER LASER BEAM, K. Obata, K. Sugioka*, H. Takai and, K. Midorikawa*, Tokyo Denki University, kanda 2-2, Chiyoda, Tokyo, Japan, *RIKEN, Hirosawa 2-2, Wako, Saitama, Japan

TiN thin films are of great use for electronic and mechanical industry for their excellent properties of high hardness, high melting point, good electric conductivity, and good diffusion barrier. Pulsed laser deposition (PLD) is a promising technique for growth of TiN. In PLD, laser fluence is one of the most important parameter to control properties of the film. Therefore, it is easily supposed that spatially nonuniform beam is unsuitable to obtain the high quality film. In the present paper, KrF excimer laser beam ($\lambda=248\text{nm}$, $\tau=34\text{ns}$) spatially homogenized by using a couple of fly's eye lenses was used to grow TiN films on Si(100) substrate. The grown films were characterized by Atomic force microscope (AFM) and x-ray diffraction (XRD), respectively. The homogenized beam drastically decreased the number of particles incorporated into the film compared with the film grown by a conventional non-homogenized beam. Additionally, the grown film had (200) preferred orientation, and rocking curve measurement of XRD indicated that the crystallinity was improved by homogenizing the beam.

- G-I/P19** SiO₂ THIN FILM PREPARATION USING DIELECTRIC BARRIER DISCHARGE DRIVEN EXCIMER LAMPS, N. Takezoe, A. Yokotani, K. Kurosawa, W. Sasaki, Dept. of Electric and Electronic Engr, Miyazaki Univ, Miyazaki, Japan; T. Igarashi, H. Matsuni, Research and Development Center, USHIO Inc., Himeji, Japan

Excimer lamps are new light sources which supply incoherent radiation in vacuum ultraviolet spectral range where laser oscillation is hard to be realized. By using a photo-chemical vapor deposition method with a Xe₂ excimer lamp (172 nm), silica film has been produced at room temperature by a single precursor process from Tetraethoxyorthosilicate (TEOS).

Transparent thin films of SiO₂ were obtained on single crystalline Al₂O₃ substrates. The deposition rate was about 0.9nm/min. The films were evaluated by means of reflection Fourier transformation-Infrared spectroscopy, scanning electron microscopy, atomic force microscopy, electron spectroscopy for chemical analysis, and ellipsometry. The film was mainly composed of amorphous SiO₂, although small amounts of residual organic materials were contained that the refractive index was 1.515 at 632.8 nm which is larger than that of bulk silica glass. The surface roughness (rms) was less than 0.5 nm. These findings indicate the VUV excimer lamp CVD is a promising method for preparing smooth, dense and fine thickness-controllable films of SiO₂ at room temperature.

- G-I/P20** REACTIVE LASER ABLATION FOR ALUMINIUM NITRIDE FILM GROWTH, A. Basillais, C. Vivien, J. Hermann, C. Boulmer-Leborgne and J. Perrière*, GREMI, Université d'Orléans, BP6759, 45067 Orléans cedex 2, France; *GPS, Université Paris 6 et 7, 2 place Jussieu, Tour 23, 75251 Paris cedex 05, France

Nitrides are being considered to be interesting materials for wear resistance coatings or high temperature and high power optoelectronic devices. The reactive laser ablation process can be an interesting way for aluminium nitride film growth. Nevertheless a deficit of N in the films is often observed and the increase of N₂ pressure during the process results in an increase of O and C impurity concentration in the film. Indeed the ablation vapor is easily contaminated by impurities via collisions with the residual gas. Moreover, it is more difficult to dissociate and ionise nitrogen in comparison with oxygen gas. Thus it seems necessary to apply some means enhancing the nitriding abilities.

In this work, a radiofrequency discharge in N₂ or NH₃ ambient gas is associated with a pulsed KrF excimer laser deposition process to study the mechanisms of reactive laser ablation leading to nitride thin film growth. The laser ablation leads to a target vapor plume plasma expanding into the ambient gas resulting in nitride radical formation in plasma phase. The time and space resolved optical emission spectroscopy diagnostic is used to investigate the nature and kinetics of plasma species for a set of experimental conditions. The correlation with the composition and structure of the deposited films will be presented and discussed.

- G-I/P21** GROWTH OF ALUMINIUM NITRIDE LAYER ON ALUMINIUM ALLOY BY EXCIMER LASER INDUCED PLASMA, E. Sicard, L. Vivet, C. Boulmer-Leborgne and C. Andreazza-Vignolle*, GREMI and CRMD* Laboratories, Université d'Orléans, BP 6759, 45067 Orléans cedex 2, France

A laser technique is used to enhance the hardness and mechanical properties of aluminium alloy (AlSi7Mg0.3). The laser beam (308 or 248 nm) is focused (1-3 J/cm²) onto the surface, the targets are located in a cell containing nitrogen (lbar). At each laser pulse (28ns), a plasma is created on the surface. After 300-500 laser pulses at the same location, a nitride layer is obtained by nitrogen diffusion into the bulk towards 5 μm depth. The nitrogen concentration depth profile is determined by a combination of different analysis, Rutherford Backscattering Spectroscopy, Nuclear Reaction Analysis, Scanning Electron Microscopy. The layer growth mechanism is not clear and the presented work is focused on this question. The laser induced plasma is responsible of nitride formation as no synthesis is observed without plasma. That means that a laser fluence threshold value is required for processing, this laser fluence corresponding to a typical temperature increase in the bulk during the laser pulse time.

A numerical calculation of the temperature profile in the alloy versus time will be presented and compared with experimental nitrogen concentration profiles to point out the correlation between temperature gradient and nitrogen diffusion. Moreover the plasma behavior during the experiment will be studied by CCD camera for different exposure times and delays from laser pulse start to determine its role in the process.

- G-I/P22** PLASMA SPECTROSCOPY FOR REACTIVE CARBON ABLATION IN NITROGEN GAS, C. Vivien, A. Basillais, J. Hermann and C. Boulmer-Leborgne - GREMI, Université d'Orléans, BP6759, 45067 Orléans cedex 2, France

This work deals with a spectroscopic study of the plasma plume in pulsed, laser deposition process applied to C_xN_y film growth. The carbon graphite ablation is produced by a KrF excimer laser beam (5-8J/cm²) in a vacuum chamber containing nitrogen or ammonia gas in the 10⁻² mbar pressure range. The experimental parameters are varied and a correlation between the plasma behaviour and the increase of the N/C concentration ratio in the C_xN_y deposited films is done.

Space and time resolved spectroscopic observations are performed using a high resolution spectrometer coupled to a fast intensified CCD camera. Plasma parameters and species kinetics are deduced from spectra analysis. Thus a tentative explanation of the different collisional mechanisms leading to the ionisation and excitation of nitrogen and carbon species is done from plasma formation (ionisation phase) to plasma expansion (recombination phase). Especially N₂, NH, N, C, C₂ and CN plasma species are investigated to point out the CN molecule formation kinetics in the expansion phase.

These informations on basic mechanisms involved in reactive laser ablation process and drawn from plasma species kinetics and gas phase reactions will be presented as a contribution to a better understanding of reactive pulsed laser deposition process applied to carbonitride thin film growth.

- G-I/P23** REACTION OF THE ZnSe SURFACE WITH CHLORINE STIMULATED BY SYNCHROTRON RADIATION, V. Stepanenko, M. Dobrotvorskaya, P. Mateychenko, I. Krasovsky, Institute for Single Crystals, 60 Lenin av, Kharkov 310001, Ukraine

The synchrotron radiation is treated as a useful tool for direct photochemical modification of surfaces. The expansion of photon energies in dry lithography technique up to VUV can lead to diminishing of the microstructure size to 100 nm and to increasing of the quantum efficiency of the reaction. In this work we have studied photochemical reaction of ZnSe with Cl₂. Cleaved surface of ZnSe crystal (110) was irradiated with VUV photons (4.5eV < E < 50eV, BESSY, Berlin) in the chlorine atmosphere (P=1 mbar) at room temperature. By means of XPS, SEM, EDS we have defined chemical composition and the thickness of the modified layer. It was shown that the reaction products formed layer of ZnCl₂, while volatile Se₂Cl₂ evaporated. Calculated quantum efficiency of reaction was about 1. A mechanism based on photodissociation of adsorbed Cl₂ and consequent Cl atoms diffusion through the products layer is proposed. Further, it was demonstrated the possibility of micro structuring at ZnSe surface by photochemical etching with the use of masks.

- G-I/P24** NEAR-THRESHOLD LASER-INDUCED SPUTTERING OF ALUMINUM SURFACE BY UV AND IR IRRADIATION, V.S. Burakov, A.F. Bokhonov, M.I. Nedel'ko, and N.V. Tarasenko, Institute of Molecular and Atomic Physics National Academy of Sciences of Belarus, 70 Scaryna Ave., 220072 Minsk, Belarus
Laser-induced particle emission (Al, Al* Al⁺, AlO) from Al and Al₂O₃ surfaces irradiated by laser beams at different wavelengths has been examined to search for primary processes of laser-initiated sputtering. The Nd-YA (1064nm, 10ns, 1-4 J/cm²), excimer XeCl (308 nm, 10ns, 0.1-0.5 J/cm²) laser or Stokes components of stimulated Raman scattering of XeCl laser radiation in pressed hydrogen (353nm, 414nm) were employed for action on the surfaces of the samples in the helium (air) atmosphere at pressures (10⁻³ - 400 Torr). The near-threshold energy fluences on the sample surface did not result in detectable surface damages but changed the surface structure and composition. LIF spectroscopy was used to detect nonemitting ground state and metastable species, while excited species was observed by time-resolved optical emission spectroscopy. The role of photochemical (electronic) and thermal effects in the initiation of particle emission have been identified in dependence on the laser wavelength. The predominance of the photochemical mechanism over the thermal one has been established in the initiation of laser-induced sputtering by radiation of excimer XeCl laser. Additionally, the resonant aspects of laser-surface-plume interaction as determined from the resonant and non-resonant irradiation of aluminum at 308.2 nm and 307.8nm have been discussed.
- G-I/P25** INFLUENCE OF THERMAL TREATMENT ON THE PROPERTIES OF THE PLASMA SPRAY DEPOSITED Ni/Al COATINGS, S. Tamulevicius, R. Dargis, A. Meskauskas, Physics Department, Kaunas University of Technology, Studentu 50, 3031 Kaunas, Lithuania; K. Slapikas, Institute of Physical Electronics, Kaunas University of Technology, 3000 Kaunas, Lithuania
Ni/Al coatings were plasma sprayed on Cu substrate at low vacuum conditions (approximately 1 Pa). The coatings were heated at temperature of 600 °C and 800 °C in Ar atmosphere for 5 hours. Scanning electron microscopy and X-ray diffraction were used to study influence of annealing on the morphology and phase transformation in the Ni/Al coatings. It was observed changing of morphology of the coatings to smoother and less porous during thermal treatment. At the same time phase transformation with appearance of new alloys took place. These changes greatly influence other properties of the Ni/Al coatings.
- G-I/P26** MODELING OF LASER ABLATION PLUME EXPANSION: AMBIENT GAS EFFECTS, VORTICES, N.M. Bulgakova, Institute of Thermophysics SB RAS, prosp. Lavrentyev 1, 630090 Novosibirsk, Russia
In this work the expansion of a plume produced by pulsed laser ablation (PLA) of solids in an ambient gas is analyzed using various model approaches. Generally, two extreme regimes of PLA plume expansion may be recognized, namely, near spherical and essentially forward directed. The spherical expansion of the PLA plume into different ambient gases is investigated theoretically using a two-fluid gas-dynamic model. Calculations show the oscillatory behavior of the plume propagation length with the amplitude strongly dependent on the background molecular weight. Simple gas-dynamic considerations based on the analogy between an ablation plume and a supersonic underexpanded gaseous jet are found to explain a number of the effects of the interaction between the plume and the background gas. The analogy predicts the vortex formation at the plume periphery due to viscous effects which is evaluated by numerical modeling using 2D Navier-Stokes equations. Flowfields obtained point to developing of the mushroom structure in the front part of the plume.
- G-I/P27** THERMAL AND PLASMA ABSORPTION EFFECTS DURING PULSED LASER ABLATION OF SOLIDS, A.V. Bulgakov, N.M. Bulgakova and S.A. Migunov, Institute of Thermophysics, prosp. Lavrentyev 1, 630090 Novosibirsk, Russia
The interaction of nanosecond Nd:YAG laser pulses with different solids (YBaCuO superconductor, graphite, niobium) and radiation absorption by laser-induced plasma plume are studied both experimentally and theoretically. In experiments, the removed mass and the radiation absorption as the functions of laser fluence are investigated by measuring correspondingly the target weight losses and the time-dependent transmission of the incident laser power through the plume. Calculations of material removal under actual ablation conditions are performed using a thermal model which describes the target heating, vaporization dynamics and plasma absorption. A method is developed to account for plasma heating due to absorption and to estimate the temperature dependence of the absorption coefficient. In this method, the plasma absorption coefficient is a function of the time-dependent fraction of the laser energy absorbed by the plasma. Calculations of the absorbed energy are compared with transmission measurements and the good agreement is obtained. The results are analysed on the basis of inverse Bremsstrahlung and photo-ionization absorption mechanisms. It is also found experimentally that increasing the ambient pressure from 0.1 to 1000 mbar leads to significantly smaller degree of transmission. The effect of background gas pressure on the absorption of laser radiation is discussed.
- G-I/P28** LASER SPUTTERING OF SOLIDS: TRANSITION FROM NORMAL EVAPORATION TO PHASE EXPLOSION, N.M. Bulgakova and A.V. Bulgakov, Institute of Thermophysics SB RAS, prosp. Lavrentyev 1, 630090 Novosibirsk, Russia
Despite the impressive successes reached in the production of thin films by pulsed laser ablation, the primary mechanisms of the vaporization of solids by nanosecond pulses of laser irradiation are still controversial subjects. There are a number of the models and qualitative considerations describing the different types of laser sputtering: normal vaporization, normal boiling, phase explosion, subsurface superheating. We have developed a model based on normal vaporization mechanism with allowance made for absorption of laser irradiation in the plasma plume. At the same time, we performed the experiments on laser sputtering of solids in a wide range of laser fluences from weak vaporization to sharp increase of mass removal which we treated as the transition to phase explosion. The comparison of the numerical and experimental data shows that this transition occurs when the surface temperature approaches the critical value. The results are analyzed in terms of the theory of critical state of the matter.
- G-I/P29** PULSE LASER REACTIVE TECHNOLOGY: GROWTH, STRUCTURE AND PROPERTIES OF TELLURIDE CADMIUM-MERCURY THIN LAYERS. B. Kotlyarchuk, D. Popovych, V. Savchuk, V. Savytski, Pidstryhach Institute for Applied Problems of Mechanics and Mathematics National Academy of Sciences of Ukraine, 3 b Naukova Street, 290601, Lviv, Ukraine
This work seeks to study the major regularities of growth processes of CdHgTe thin layers at laser beam evaporation ($\lambda=1.06 \mu\text{m}$, $\tau=15 \text{ ns}$, $q=(5-7) \times 10^7 \text{ W/cm}^2$) and condensation on the substrates in a chemically active medium and their influence on the properties of these layers. For conservation of the stoichiometry on condensed films under conditions of intensive re-evaporation of mercury at epitaxial growth temperature ($T_s=220-240 \text{ }^\circ\text{C}$) we suggest the method, that makes it possible to carry out the laser evaporation and condensation of vapour into the quasi-closed reaction space. The pressure of mercury vapours into this space is equal to $P_{\text{Hg}}=10^{-1}-10^{-3} \text{ Torr}$. It is determined that the CdHgTe layers with different carrier concentration and necessary conductor type may be formed in a reaction chamber, depending on the substrate temperature and the mercury vapour pressure into the reaction chamber. This technology makes it possible to form the multilayered p-n-junctions (separately sandwich-photoreistors). The recombination barriers are available in this multilayers. The recombination barriers causes the decrease of free carrier concentration and their life time increase. In this case only photoelectrons realize the conduction modulation, they are unfundamental carriers. It does not specify high requirements to critical low concentrations of fundamental carriers in the film structures, that are really formed.

G-I/P30 VELOCITY DISTRIBUTIONS OF PARTICLES PRODUCED BY LASER ABLATION OF SILICON AND THEIR INTERPRETATION IN TERMS OF ABLATION MECHANISMS, A.V. Bulgakov, O.F. Bobrenok and M.R. Predtechensky, Institute of Thermophysics, prospect Lavrentyev 1, 630090 Novosibirsk, Russia

The neutral constituents of the plasma plume generated during pulsed ablation of silicon by frequency-doubled Nd:YAG laser radiation (532 nm) both in vacuum and ambient gas are studied in order to provide a better understanding of ablation mechanisms. The velocity distributions of plume particles (atoms and small clusters) are investigated for different laser fluences using time-of-flight mass spectrometry. At low fluence (below 1 J/cm²), a narrow distribution at around 5 km/s is measured in vacuum for Si atoms. This low-fluence atom emission is attributed to non-thermal evaporation process. As laser fluence increases, the slower and broader distributed atoms appear in the plume due to thermal ablation mechanism resulting in a two-component velocity distribution. There occurs a gradual transition from non-thermal to thermal evaporation, and at about 3 J/cm² thermal mechanism dominates. At moderate fluences, when thermal ablation contributes appreciably, the neutral Si clusters (up to 8 atoms per cluster) with near-Maxwellian velocity distribution peaking at around 2 km/s are registered. The fraction of clusters is found to increase strongly with increasing the ambient gas pressure. The observed clusters appear to be formed mainly by gas phase collisions of those Si atoms which are emitted via thermal ablation mechanism.

G-I/P31 SR STIMULATED REACTION OF GaAs WITH Cl₂:STUDY OF REACTION PRODUCTS, V. Stepanenko, M. Dobrotvorskaya, Institute for Single Crystals, 60 Lenin av., Kharkov 310001, Ukraine, and U. Sterller, H. Raaf, N. Schwentner, Institut für Experimentalphysik, FU Berlin, Arnimallee 14, 14195 Berlin, Germany

It's well established that VUV emission strongly enhances chlorine assisted etching of GaAs wafers revealing quantum efficiencies far above unity and giving thus a versatile tool to produce structures of 100 nm dimensions. In the present work performed at BESSY storage ring we investigated the wavelength dependence on reaction process. All exposures have been made with constant Cl₂ pressure of 1 mbar at room temperature. CaF₂ and LiF filters were used to cut the emission limited to 122 nm and 105 nm, correspondingly. A lack of AsCl_x containing products was observed which is attributed to high volatility, while GaCl_x containing products form layer on top of GaAs. The layer exposed with 105 nm cut-off emission is 10 times thicker (300 nm) compared to those exposed with 122 nm cut-off (30-40 nm). The reaction efficiency derived from the etching depth profile is not depending on wavelength. Supposing that adsorption of chlorine does not depend on wavelength, we discuss possible mechanism for the reaction. It is proposed that shorter wavelength part can enhance strongly the penetration of Cl atoms into the depth of products layers and/or suppress desorption of GaCl_x. Photodissociation of Cl₂ adsorbed layer and formation of Cl atoms with excess kinetic energies of several eV is supposed to be the reason for the first process, while more effective Ga and As diffusion from the bulk GaAs supports the second one.

G-I/P32 PLASMA STIMULATED REDISTRIBUTION IMPURITIES IN Si AND ITS APPLICATIONS, A.N. Buzynin, A.E. Luk'yanov, V.V. Osiko, V.V. Voronkov, General Physics Institute of RAS, 117942, 38 Vavilov st., Moscow, Russia

It was shown [1] that p-Si irradiation by low energy Ar ions at room temperature leads to the redistribution of the impurities in Si. If Ar irradiation is used during 1-15 min the redistribution of impurities is essential only nearby the subsurface defects. So the treated samples may be used to investigate the electrical activity of subsurface defects in SEM EBIC mode with high sensitivity (improvement is more than an order of magnitude). More duration of treatment leads to the inversion of conductivity and p-n junction formation. The surface and bulk defects were clearly visualized by using SEM EBIC technique as the form of this p-n junction distorted on the defects. The junction displacement velocity either decreases if some defect is located on the surface or just beneath it or increases if any defect is in the p-n junction way. So the sensitivity of SEM EBIC technique (and some other techniques too) in Si sample defect revealing is much higher if one uses above mentioned p-n junctions. One can provide the higher revealing degree either electrically active bulk defects and inhomogeneities or subsurface defects or mechanical treatment surface defects by changing the ion treatment conditions.

I.A.N.Buzynin, A.E.Luk'yanov, V.V.Osiko, V.V.Voronkov. MRS Symp.Proc. 1995. V.378. P.653-658.

G-I/P33 UV ETCHING ACCOMPANIED BY MODIFICATIONS, N. Bityurin, Institute of Applied Physics Rus. Ac. Sci., 46 Ul'janov str., 603600, Nizhnii Novgorod, Russia

The kinetics of UV light material modification is considered. This modification proceeds through several photochemical-like reactions, which significantly change optical properties of material. The analytical solution of this problem is reviewed. The symmetry of this solution allows obtaining the solutions of some other problems where the modification of material is accompanied by its etching.

Two limiting cases are studied from this general point of view. The first one is the surface etching. Here etching velocity depends explicitly on light intensity and on the concentrations of modification products at the very surface. In this case it is possible to reduce the problem rigorously to the set of ordinary differential equations and to follow the modifications and etching kinetics for arbitrary time dependence of intensity for general nonstationary case.

The other limiting case is bulk etching. Here the change in film thickness is caused by the bulk photochemical reaction. The analytical solutions for time dependence of the surface position and of spatial distribution of modification products are obtained in a quite general form.

The theoretical results are compared to the recent experimental data on UV modifications of polymer films.

G-I/P34 AFM AND MICROSTRUCTURE STUDIES OF IMPLANTED CARBON IN SILICON UPON EXCIMER LASER ANNEALING, W. Wu, D.H. Chen, J.B. Xu, S.P. Wong, I.H. Wilson, Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong

Synthesis of silicon carbide (SiC) and diamond-like structures has been achieved by carbon ion beam implantation into Si wafers with various ion implantation doses. Subsequently, excimer laser annealing has been carried out in vacuum at various energy densities with single pulses. Rutherford backscattering spectrometry (RBS) reveals carbon redistribution after the annealing procedure. Infrared spectra and X-ray diffraction spectra (XRD) were used to analyze the microstructures. The influence of carbon implantation dose and exposed laser energy densities on the surface morphology are studied by atomic force microscopy (AFM), it shows columnar grains with a mean size of twenty nanometers are distributed all over the irradiated sample surface. For laser annealing of high dose carbon implantation (1.2x10¹⁸) samples, Raman spectra show the peaks from 1400 to 1600 cm⁻¹ and 800 cm⁻¹ which corresponding to the diamond-like and 3C-SiC species, respectively.

G-I/P35 SURFACE MODIFICATION OF GaAs SINGLE CRYSTALS BY LASER INFRARED LIGHT, P. Kosoboutski, A. Danylov, The University L'vivska Politechnika, 12 Bandery Str., 290646 Lviv, Ukraine

The effect of laser irradiation (wavelength $\lambda=1.06\mu\text{m}$, mean laser power $P=25\text{W}$, diameter of laser spot $d=20\mu\text{m}$, time of effect $t=600$ seconds) on the concentration distribution of Ga and As atoms at the surface of GaAs single crystals is studied. It was determined by the x-ray microanalyzer method, that in the irradiated surface regions the concentration of Ga atoms increases and one of As atoms accordingly decreases due to sublimation from the surface. The obtained result can be perspective in technology of metal-semiconductor ohmic contact fabrication at GaAs surface, that is important for microelectronics.

- G-I/P36** MONTE-CARLO SIMULATION OF ABOVE-SURFACE NEUTRALIZATION OF HIGHLY CHARGED IONS, M.N. Mirakhmedov, R.A. Salimova, Institute of Electronics, 700143 Tashkent, Uzbekistan
A thermonuclear plasma can contain highly charged ions (HCI) of admixed atoms. In this connection the investigation of HCI interaction with the surface is of interest.
In the present work, a program simulating the above-surface neutralization of HCI was developed. By method Monte-Carlo the processes occurring at the approach of HCI to the surface are run, namely: resonant capture of electrons from the conduction band into excited outer shells of the HCI; Auger transitions of captured electrons into deeper shells; resonant loss of electrons which have been shifted above the Fermi level of target surface. The emission of electrons promoted above vacuum level and acceleration of HCI due to its image charge attraction are taken into account.
The results of calculations for neutralization of C^{+6} on the surface of carbon have shown that significant part of neutralization energy is transferred to electrons of conduction band at resonant loss of electrons into empty states of conduction band and at emission into vacuum by promotion of captured electrons.
- G-I/P37** TEA-CO₂ LASER INDUCED DAMAGE OF TiN AND (TiAl)N COATINGS, B. Gakovic, M. Trtica, T. Nenadovic and T. Grdic, Institute of Nuclear Sciences Vinca, PO Box 522, 11001 Belgrade, Yugoslavia
High-hardness coatings and their behaviour during different beam bombardment are of great fundamental and technological interest. In this work the changes induced by laser beam on TiN and (TiAl)N coatings were considered.
Coatings were deposited by sputtering. The bombardment of coatings was performed with TEA-CO₂ laser operating in multimode regime with fluence 7-80 J/cm². The coating properties and damages after 10-340 pulses are analysed by SEM and XRD.
The results have shown that the morphological features and damages induced during interaction depend on the pulse intensity, the pulse shape and chemical composition of deposits. Tail-free (FWHM=80ns) and pulses with tail (FWHM=120ns, tail=2μs) produced intensive damages. The photo deposition sputtering yield is a function of laser beam power density and target characteristics. Our results suggest that this conclusion should take into account the pulse shape.
- G-I/P38** UV LASER INTERFACIAL SYNTHESIS OF CN-BCN LAYERS ON DIAMOND FILMS IN BORAZINE AND AMMONIA, M. Ugarov, V. Ageev, A. Karabutov, E. Loubnin, S. Pimenov, V. Konov, Natural Sciences Center of General Physics Institute, 38 Vavilov str., 117942 Moscow, Russia, and A. Bensaoula, University of Houston, Space Vacuum Epitaxy Center, SR1, 4800 Calhoun, Houston Texas, USA
The application of CVD polycrystalline diamond films implies the comprehension of the role of the intergrain glassy carbon component and the chemical state of film surface in the formation of the electron properties. A search for methods to reproducibly modify these parameters becomes of critical importance in order to develop applications for these important class of materials.
Our studies show that UV laser induced thin film synthesis of various nitride layers can be easily realized using a modified CVD method. A series of experiments are reported on the effect of ArF laser irradiation of nanocrystalline diamond films in borazine (B₃N₃H₆) and ammonia (NH₃) atmospheres. It is shown that below the graphitization threshold, the pulsed UV laser irradiation may result not only in B and N atoms intergrain penetration into the film bulk accompanied by chemical reactions with intergrain nanocrystalline graphite, but also in the surface synthesis of continuous ultra thin layers of ternary B-C-N (if processed in borazine) or sp² bonded C-N compounds (in ammonia).
The mechanism of the observed effects as well as their influence on the electron properties of diamond film surfaces is discussed.
This material is based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. RE1-247, an Texas Advanced Research Program (ARP#1-1-27764), and a NASA cooperative agreement (#NCC8-127).
- G-I/P39** LASER-DRIVEN PLASMA CVD OF CN/BN COMPOUND FILMS, V. Ageev, M. Ugarov, E. Loubnin, V. Konov, Natural Sciences Center of General Physics Institute, 38 Vavilov str., 117942 Moscow, Russia, and A. Bensaoula, N. Badi, A. Tempez, and D. Starikov, University of Houston, Space Vacuum Epitaxy Center, SR1, 4800 Calhoun, Houston Texas, USA
1. Effects of TEA CO₂ laser induced plasma CVD of CN/BN compound films are reported for the first time.
A new method of plasma CVD of CN/BN films at the dielectric optical breakdown of CH₄/N₂ and BCl₃/N₂-based gaseous mixtures above substrate surfaces by pulsed IR radiation from a TEA CO₂ laser is discussed.
The composition and structure of the films as a function of the main deposition parameters (substrate temperature, laser intensity, vapor pressure and percentage) were studied by methods of Raman and X-ray photoelectron spectroscopy.
The realization of amorphous near-stoichiometric CN thin film synthesis with a significant sp³ C-N bonds content is demonstrated. The laser induced plasma CVD of h-BN film is also realized under a wide range of experimental conditions. The thin film properties obtained by the above method are compared to CN/BN films generated by ion-assisted ECR and traditional plasma CVD.
The implication of these results on synthesis of ternary B-C-N compound films using a similar laser enhanced process will be discussed.
2. Preliminary results on excimer laser annealing of CN films under vacuum conditions and in nitrogen-containing gaseous environments are reported. The sp³-sp² transition in CN film are shown to be the primary result of laser irradiation - the process being very similar to the graphitization of diamond and diamond-like carbon films. Some aspects of possible laser controlled variation of C_xN_y content are also discussed.
The processes enable one to form electrical conducting patterns in amorphous CN films as well as to vary their chemical stability. In particular, our results open new possibilities for selective area processing of CN films (e.g. via a chemical dry plasma etching, etc.)
This material is based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. RE1-247, an Texas Advanced Research Program (ARP#1-1-27764), and a NASA cooperative agreement (#NCC8-127)
- G-I/P40** NON-LINEAR LASER TRANSIENT PHOTOCONDUCTIVITY IN BORON NITRIDE FILMS, S. Klimentov, V. Ageev, E. Loubnin, M. Ugarov, S. Garnov, General Physics Institute, 38 Vavilov str., 117942 Moscow, Russia, and A. Bensaoula, N. Badi, A. Tempez, and D. Starikov, University of Houston, Space Vacuum Epitaxy Center, SR1, 4800 Calhoun, Houston Texas, USA
The steadily growing interest in BN films is determined by the unique sum of the material properties and by the recent progress in the synthesis of high quality films of desired composition. Device implementation of BN-based planar structures in semiconductor electronics (high voltage switches, radiation detectors, etc.) requires a detailed characterization of the electronic properties of these thin films and the free carrier dynamics in particular.
In the present work results of laser transient photoconductivity (PC) studies of BN films are reported for the first time. A selection of sub-micron carbon-doped mixed cBN/hBN films generated by ion-assisted ECR-plasma CVD was analyzed. Film structure and composition were characterized by XPS, EPMA, XRD, FTIR and Raman spectroscopy.
Efficient excitations of films were demonstrated by using nanosecond radiation pulses of the 2nd, 4th harmonics of Nd:YAG laser. The PC-sensitivity is shown to be tremendously determined by the nitrogen deficiency and the carbon doping level, both being responsible for the generation of donor/acceptor levels in this system.
The observed PC-signal behavior is an evidence of a cascade excitation process in these BN films via the 2-3 photon (wavelength dependent) population of a series of donor levels with their subsequent single quantum ionization to the conduction band.
Unusual PC-signal enhancement via additional post growth modification of the films is discussed.
This material is based upon work supported by the U.S. Civilian Research and Development Foundation under Award No. RE1-247, an Texas Advanced Research Program (ARP#1-1-27764), and a NASA cooperative agreement (#NCC8-127)

SYMPOSIUM G

- G-I/P41** COMPUTER MODELLING OF STATISTICAL CHARACTERISTICS OF NITROGEN LASER IMPULSE IN NONLINEAR MEDIUM, V.A. Kazartcev, N.V. Brazovskaya Altai State Technical University, Lenin-street 46, box-524, 656061 Barnaul, Russia

The main purpose of modelling of the work of laser arrangement according to the classical scheme generator-moulder-amplifier is investigation of behavior of impulse of optical radiation passing through non-linear medium.

Modelling is based on imagining the electrical field as a complex Gauss process with a correlation function: $\gamma(\tau) = e^{-\tau/\tau_k}$, $\tau_k = 0.2 \cdot 10^{-9}$ sec - experiment cogeneration time for nitrogen laser with a drop impulse form. With the help of Fourier transformation according to frequencies we find randomize physical spectrum of impulse from which we can "get" different characteristics. Receiving statistical medium of the spectrum we can have its form which gives us an opportunity to compare the modelling results with the experimental results.

Characteristics which are of interest from the point of view of reliability of receiving experimental results are examined. As a rule the spectrum is fixed by the devices which have limited zoned of registration. Thus it is possible to measure the location of spectrum components relatively to each other. For carrying out reliable analyses of modelling and experimental results it is required to receive characteristics which connect the intensity of radiation with the location of spectrum components relatively to each other. Thus the following characteristics are regarded: distribution of intervals among neighbouring spectrum components, distribution of spectrum components according to their intensity, characteristic of spectrum somewhat periodicity. The zone of registration is taken into consideration with the help of some level definition, lower of which the components are invisible.

- G-I/P42** LASER DEPOSITION OF SEMICONDUCTING THIN FILMS FROM $\text{Fe}(\text{CO})_5$ VAPORS, S.A. Mulenko, M.M. Nishchenko, Institute for Metal Physics NAS of Ukraine, 252680 Kiev, Ukraine and V.S. Ovechko, Kiev Taras Shevchenko University, 252127 Kiev, Ukraine

Laser chemical vapor deposition (LCVD) method was applied for the formation of thin semiconducting films while deposition of elements from iron carbonyl ($\text{Fe}(\text{CO})_5$) under the action of Ar+ laser radiation (~ 488 nm). The deposition rate of films was about 0.8 Å/s on Si substrate and vapor pressure of 5 Torr at the laser power density of 10^2 W/cm². The thickness of deposited films was about 250 Å. Measurement of specific conductivity of such film in the temperature range (77-287)K showed their typical semiconducting trend: (7.7-17.5) $\Omega^{-1}\text{cm}^{-1}$. Bind energy of carriers (electrons or holes) with impurity (E_i) of this film was about 0.01 eV. These semiconducting properties are dealt mainly with iron oxides (FeO , Fe_2O_3) formation. Irradiation of deposited film with focused of YAG: Nd³⁺-laser radiation at the power density of 2.6×10^3 W/cm² resulted in increasing of E_i up to 0.1 eV owing to the formation of new semiconducting phase $\text{FeSi}_{2-x}\text{C}_x$ in the surface layer of Si substrate. The highest sensitivity of this semiconducting element was about 0.3 mA/V. That makes it perspective as energy converter in the IR range of spectrum.

- G-I/P43** LASER-INDUCED RADIATIVE RISING OF DEFECTS ON TO SURFACE AND METAL SURFACE DESTRUCTION, A.F. Banishev, V.Ya. Panchenko, A.V. Shishkov, NICTL - Laser Research Center Center for Technological Lasers of Russian Academy Science, 140700 Shatura, Moscow Region, Russia

The paper presents the experimental results of investigation into the processes of radiative drift of structural defects (vacancies, dislocations, pores) in the field of thermoelastic stresses generated in non-transparent solids (metals) under powerful laser pulses. It is known that: defects can emit radiative quanta during their formation or movement in the field of elastic stresses. The intensity of this emission (mechanoluminescence - ML) is largely governed by the density and velocity of defects, which, in their turn, depend on the velocity of thermoelastic stresses build-up in the sample as the result of laser action. The spectral composition and temporal dependence of ML intensity have a rather complicated form, and, as far as we know, there is not a universally accepted model, particularly for metals, that could describe the mechanism of photon emission during the generation and movement of defects, as well as the dependence of glow intensity on defects concentration, temperature and elastic stresses. The paper presents the results of the study of structural defects radiative rising to the surface of polycrystalline W and Mo samples. The spectral composition and glow kinetics of individual spectral ML, lines was investigated under thermoelastic stresses induced in them by Nd:YAG laser pulses.

Wednesday June 17, 1998
 Mercredi 17 juin 1998

Afternoon
 Après-midi

Poster Session II
 17:30-19:00

- G-II/P1** PULSED LASER REACTIVE ABLATION OF III GROUP ELEMENTS IN AMMONIA ATMOSPHERE: PHOTOIONIZATION THRESHOLDS AND STRUCTURES OF $\text{Me}(\text{NH}_3)_n$ CLUSTERS, T.M. Di Palma, A. Latini, M. Satta, A. Giardini Guidoni, Dipart di Chimica, Univ. "La Sapienza", P.le A. More 5, 00185 Roma, Italy
 The study of clusters has received much attention in recent years due to the peculiarities of this state of matter as intermediate between isolated gas and condensed phases. A photoionization study of the III group metal-ammonia clusters formed in the reaction of photoablated metal vapour with gaseous ammonia and expanded in a supersonic beam is here reported. The ionization potentials (IPs) of $\text{Me}(\text{NH}_3)_n$ clusters have been measured. The cluster IPs are shifted at lower energies compared to the bare atom, and they decrease almost monotonically with increasing cluster size. This trend appears to confirm, also for these systems, a delocalization of the metal valence electron in the cluster surface state. For small clusters the difference between the binding energy of the ion and the difference between the binding energy of the ion and the neutral complexes is compared with energetics calculated by a density functional method. A detailed analysis of the bonding mechanisms shows that molecular stability is quite high confirming our previous hypotheses that these complexes can be gaseous precursors in the nitridation process.
- G-II/P2** REACTIVE ION ETCHING OF CoSi_2 IN CF_4/Ar PLASMA, G. Beddies, M. Falke, S. Teichert, B. Gebhardt, H.-J. Hinneberg, Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany
 The formation of polycrystalline silicides by the reaction of thin metal films with silicon has wide application in the semiconductor industry. For further developments epitaxial silicide films have the advantage of the absence of grain boundaries and consequently of better thermal stability, lower electrical resistivity and a smoother interface.
 The solid phase reaction of metallic bilayers (e.g. Co/Ti) with Si(100) during an RTA process is a new non UHV method to grow epitaxial CoSi_2 film on Si(100). Finally on top of the epitaxial CoSi_2 layer one or several in composition and thickness varying silicide layers are formed depending on temperature and time of the RTA process.
 An RIE plasma process has been developed to remove these top layers. The etching rate in a CF_4/Ar plasma was 1... 10 nm/min depending on rf power and the structure of the top layers. The in-situ characterisation of the plasma process has been performed by laser interference, Langmuir-probe measurements and mass-spectrometry. The thicknesses of the etched films have been determined by sheet resistance measurements, RBS and TEM. The surface morphology was investigated by REM, TEM and AFM.
 The CF_4/Ar plasma etching process can also be used to pattern thin CoSi_2 films.
- G-II/P3** WC-Co CUTTING TOOL SURFACE MODIFICATIONS INDUCED BY PULSED LASER TREATMENT, E. Cappelli, F. Pinzari, P. Ascarelli, CNR-IMAI, P.O.B.10, 00016 Monterotondo Scalo, Roma, Italy, and S. Orlando, CNR-I.M.S., Zona Ind. di Tito Scalo, 85050 Tito Scalo, Potenza, Italy
 Many innovative industrial materials like carbon fibers, metal matrix composites (MMC), hypereutectic Al/Si alloys are very hard and difficult to machine with traditional cutting tools. CVD diamond coated inserts seem to be the most promising system to overcome the problem. The WC, xCo hard metal, a widespread used and cheaper bulk material, could be a convenient substrate for diamond film coatings. The Co-rich binder phase, however, constitutes a severe obstacle for diamond deposition and adhesion, owing to its catalytic effect for amorphous carbon or soot formation. Several chemical and physical methods have been developed to etch Co from the surface; however, no definite and reliable procedure has been achieved.
 In our experiments, we treated the WC, xCo hard metal substrates with ArF ($\lambda=193$ nm, $h\nu=6.4$ eV) and CO_2 ($\lambda=10.6$ mm, $h\nu=0.12$ eV) pulsed lasers, at different fluences and incident angles, to modify both the chemical composition and the structure of the surfaces. The morphological and chemical effects have been studied by XRD, SEM/EDAX microscopy and XPS surface analysis. Surface roughness modifications have been observed and quantified by AFM. Diamond nucleation and adhesion are compared with results obtained on the plain tool substrates.
- G-II/P4** CHARACTERIZATION OF a-SiN:H FILMS DEPOSITED BY ArF LASER PHOTOLYSIS OF DISILANE AND AMMONIA, N. Banerji, J. Serra, S. Chiussi, F. Lusquinos, B. Leon, M. Perez-Amor, Departamento de Fisica Aplicada, Universidad de Vigo, Lagoas Marcosende 9, 36207 Vigo, Spain
 Silicon rich silicon nitride films have been obtained through ArF laser-induced photolysis of $\text{Si}_2\text{H}_6/\text{NH}_3/\text{Ar}$ gas mixtures. High growth rates ranging from 200-500 Å/min results from the combined photolysis of disilane and ammonia and its variation has been studied as a function of the substrate temperature, total pressure, and $\text{Si}_2\text{H}_6/\text{NH}_3$ ratio. While the growth rate undergoes a linear rise with the substrate temperature and gas ratio, its variation with the total pressure shows a decrease from 2-6 Torr which is followed by an increase up to 9 Torr. An explanation for this variation based on the reactive photofragment concentrations, secondary photolysis and substrate nucleation, has been given. These films behave like wide band-gap semiconductors with their optical band gap (E_g) found from the Tauc plot ranging from 1.7-2.4 eV and it can be systematically tailored with the deposition parameters. In all films a direct dependence has been observed between the extent of bonded hydrogen and E_g .
- G-II/P5** USE OF A DUPLEX PLASMA PROCESS FOR THE IMPROVEMENT OF CORROSION RESISTANCE OF STEEL, L. Mouri, I. Mabilie, C. Fiaud, J. Amouroux, Laboratoire de génie des procédés plasmas et traitements de surface (ENSCP), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
 This paper deals with the improvement of the hardness and corrosion resistance of commercial steel samples using a plasma process. The method used in the process is a duplex treatment in an inductively coupled plasma reactor with a radio-frequency generator (40MHz). The treatment itself is decomposed into two parts; after ion cleaning, first we use a Nitrogen-Hydrogen (25%-75%) plasma to proceed at the surface nitriding then we use a Methane-Hydrogen (5%-95%) plasma to proceed at the surface carburizing. The surface properties of the treated samples were compared with untreated ones. Different electrochemical techniques were used to evaluate the corrosion resistance of the samples and the nature of the surface layer was studied by XPS. It appeared clearly that the plasma process improves hardness and corrosion resistance of the steel samples. The highest protection rate obtained is 99.6% relatively to the non-treated steel and the hardness is increased from $\text{HV}_{30\text{kg}}=280$ to $\text{HV}_{30\text{kg}}=540$. The studied parameters were the time treatment, the gaseous flow rate and the power produced by the generator during each step of the duplex treatment. AFM figures and SEM micrographs show the formation of a uniform structure on the surface. The surface rugosity is increased by the plasma treatment. XPS measurements show an enrichment in nitrogen and carbon and the presence of oxygen.

SYMPOSIUM G

- G-II/P6** **LASER MODIFICATION OF MATERIAL SURFACE PROPERTIES FOR IMPROVED WETTABILITY AND ADHESION**, J. Lawrence, L. Li, Manufacturing Division, Department of Mechanical Engineering, University of Manchester Institute of Science & Technology (UMIST), PO Box 88, Manchester, M60 1QD, UK; J.T. Spencer, Research & Technology, B709, BNFL, Springfields Works, Salwick, Preston, PR4 0XJ, UK
To date, very little work has been published with regard specifically to the use of lasers for modifying surface properties of materials in order to improve their wettability and adhesion characteristics. Work has been conducted using a 60 W-cw high power diode laser (HPDL) in order to determine the effects of HPDL radiation on the wettability characteristics of certain ceramic and metallic materials, with specific regard to surface coating applications or enamelling applications. Through experimentation it was found that laser treatment of the materials surfaces reduced the surface energy and accordingly, wetting experiments, by the sessile drop technique, revealed that laser treatment of the materials surfaces resulted in a decrease in the contact angles. The work shows clearly that laser radiation can be used to alter the wetting and adhesion characteristics of a number of materials by means of changing the surface energy.
- G-II/P7** **MODELING AND DYNAMIC SIMULATION OF ULTRAVIOLET INDUCED GROWING INTERFACES**, J. Flicstein, E. Guillonnet, S. Pata, L.S. Kee Chun, J.F. Palmier, J.L. Courant, FT, CNET, DTD, Laboratoire de Bagneux, 92225 Bagneux, France
Many challenging problems are associated with ultraviolet patterns induced deposition. For III-V semiconductor substrates, the interest is motivated by the possibility to describe the UV deposition process of an insulator for passivation. A model is proposed for the three-dimensional time evolution of the profile of a growing interface. It is recognized that the nucleation process occurs at an UV induced active charged center on the surface of the substrate with scaling properties[1]. The model includes lattice co-ordination and atom-atom interactions out to third-nearest neighbours. Molecular dynamics processes are taken into account using energy barriers. The activation energy depends on the configuration of neighbouring atoms. The events are chosen with a probability of occurrence that depends on the kinetic rates at each site. Three dimensional simulation of deposition provides a framework for experimental measurements and validation in scaling nanometric photodeposition processes.
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- G-II/P8** **A NOVEL METHOD FOR LASER INDUCED PERIODIC DOMAIN REVERSAL IN KTP**, K. Daneshvar, Electrical Engineering Department, University of North Carolina, Charlotte NC 28223, USA
It has been demonstrated that an intense laser light in conjunction with a strong localized field can be used to reverse the polarity of the ferroelectric domain at the location of a laser beam[1]. It has also been shown that an optical waveguide by ion diffusion can be induced by using a laser beam[2]. Using these two methods we have developed a technique to construct nonlinear periodic structure in an optical waveguide that can be used for phase matched second harmonic generation (SHG). The applications of such waveguides are well documented in the literature[3].
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- G-II/P9** **NITRIDATION OF ZIRCONIUM IN NH₃ PLASMA**, A. Straboni, L. Pichon, T. Girardeau, M. Drouet, Laboratoire de Métallurgie Physique, Université de Poitiers, SP2MI, UMR 6630 CNRS, BP 179, 86960 Futuroscope cedex, France and J. Perrière, Groupe de Physique des Solides, Université Paris VI, tour 23, 2 place Jussieu, 75251 Paris cedex 05, France
Due to its high hardness, high thermal stability and its interesting electronic properties, the stable Zirconium nitride (ZrN) phase has motivated recent experimental research using mainly deposition techniques. Thermal growth in a reactive plasma presents several advantages over deposition such as isotropic layer growth, gradual interface between film and substrate and production of very stable structures. Nitrided layers were grown on thin Zr films deposited on Si and on massive Zr immersed in a low pressure NH₃ plasma. The plasma was created in a quartz tube using 13.56 MHz excitation and the sample temperature was controlled between 600-800°C by an outer furnace. The growth of the nitrided layers and their physical properties were studied using Rutherford backscattering, Auger profiling and in-situ ellipsometry. The kinetics of nitrogen incorporation show that N transport in the sub-surface was strongly influenced by the plasma. The surface layer was shown to be stoichiometric ZrN with a stabilized structure as shown by EXAFS experiments.
- G-II/P10** **KINETIC STUDY OF 222 NM EXCIMER LAMP INDUCED DECOMPOSITION OF PALLADIUM-ACETATE FILMS**, Z. Geretovszky and I.W. Boyd, University College London, Department of Electronic and Electrical Engineering, Torrington Place, London WC1E 7JE, UK
Wavelength selectivity, high intensity, long lifetime and low maintenance cost make excimer lamps a popular UV source for large area processing. Photo-induced metal seeding followed by electroless plating is just one area where the use of these efficient light sources can contribute to the development of new techniques aimed at reducing the processing temperature. Although, the use of palladium-acetate to produce Pd seed layers has already been studied with various energy sources, including excimer lasers and lamps, the details of the photochemical mechanisms involved are still unexplored. In this paper the kinetics of 222 nm KrCl* excimer lamp initiated palladium-acetate decomposition are presented. The species ejected from the irradiated films were monitored in situ by mass spectrometry at ultra high vacuum. Interpretation of the time evolution of multichannel mass spectrometric data, together with complementary infrared, UV-visible and X-ray photoelectron spectroscopic characterization has led to an understanding of the governing physical and chemical mechanisms which are described here for the first time.
- G-II/P11** **PLD - AN ALTERNATIVE ROUTE FOR THE GROWTH OF MAGNETIC THIN FILMS**, A.G. Jenner, L. Stone, J. Hayes, H.V. Snelling and R.D. Greenough, Department of Physics, University of Hull, Hull, HU6 7RX, UK
For many years there has been considerable interest in producing thin films of magnetic materials in order to reduce the size and/or enhance specifications of devices for passive or active applications. The need for new, high performance, materials occurs for example in magnetic recording (i.e. increased recording densities) and microactuation and sensor technologies.
Microstructure, composition and magnetic properties of thin films produced by Pulsed Laser Deposition (PLD) from the following soft magnetic systems have been studied Fe, Fe₉₀Zr₁₀, TbFe₂, DyFe₂ and Tb_{0.3}Dy_{0.7}Fe_{1.95}. All these materials display sensor or actuator properties in the bulk have been studied. Two PLD systems were used to produce the thin films. Firstly, a TEA CO₂ laser ($\lambda = 10.6 \mu\text{m}$, 90ns FWHM pulse duration) and secondly an ArF Excimer laser ($\lambda = 193\text{nm}$, 16ns FWHM pulse duration). The effect of varying deposition parameters e.g. fluence, and post production processing has been investigated. Deposition conditions have been established that give low droplet densities with the best quality films being Fe deposited by TEA CO₂ laser irradiation. In-plane strains in the region of 75 - 300 ppm at 1 MAm⁻¹ have been observed for both DyFe₂ and TbFe₂ grown on quartz cantilevers from rotating and stationary targets. Similar thickness Tb_{0.3}Dy_{0.7}Fe_{1.95} films have displayed in-plane longitudinal strains of 400 - 830 ppm at 1 MAm⁻¹.

- G-II/P12** DUV LASER INDUCED DEPOSITION OF a-C:H FROM CH₂I₂ AT ROOM TEMPERATURE, M. Lindstam, M. Boman, Uppsala University, Ångström Laboratory, Department of Inorganic Chemistry, Box 538, 75121 Uppsala, Sweden and K. Piglmayer, Johannes Kepler University, Institute of Experimental Physics, Department of Applied Physics, 4040 Linz, Austria
Amorphous carbon films have been deposited at room temperature by photolytic dissociation of CH₂I₂. A Ar⁺ laser operating at 275-305nm (DUV) was used as excitation source. The laser beam was focused above and in parallel to the Si(100) substrate surface. The deposition process was investigated as function of laser power, gas flow rate, laser-beam-to-substrate distance and gas pressures. The films were analyzed by Raman spectroscopy, atomic force microscopy, and energy dispersive X-ray spectroscopy. Optimum deposition conditions were obtained at close beam-to-surface distances.
- G-II/P13** GROWTH OF DOPED CRYSTALLINE Y₂O₃ THIN FILMS BY P.L.D. FOR LASER WAVEGUIDE, A. Aron, A. Huignard, J. Thery, L.C.A.E.S. UMR-7574, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France; J. Perriere, A. Laurent, G.P.S., Univ Paris VII, URA-17, Tour 23, 2 place Jussieu, 75251 Paris Cedex 05, France
Thin films, used as laser waveguide, present the advantage, compared to bulk laser, to reduce the laser threshold. This requires a high crystalline quality. Laser ablation appears therefore a very suitable method. We report here the growth of undoped and Ln³⁺-doped Y₂O₃ thin films (Ln = lanthanide). This material, well known as a host lattice for rare earth luminescent ions, presents a difficult crystallisation by other methods, because of its high melting point. However doped Y₂O₃ is a relevant laser material. The films were grown on (100)-oriented MgO and Si single crystal substrates. By the complementary use of Rutherford backscattering spectrometry, X-ray diffraction and electron microscopy analysis, the composition, structure and surface morphology of the films were studied as a function of substrate temperature. Textured films of undoped Y₂O₃ with (111) orientation were grown on MgO substrate with high crystalline quality, as shown by RBS in channeling geometry. Doped Y₂O₃ films were also grown. These results will be presented and discussed.
- G-II/P14** A COMPARATIVE REVIEW OF THE EFFECTS OF LASER WAVELENGTH ON LASER CLEANING OF CHLORINATED RUBBER, M.J.J. Schmidt, L. Li, Manufacturing Division, Department of Mechanical Engineering, University of Manchester Institute of Science and Technology (UMIST), PO Box 88, Manchester, M60 1QD, UK; J.T. Spencer, Research & Technology, B516, BNFL, Springfields Works, Salwick, Preston, PR4 0XJ, UK; P.H. Key, Department of Applied Physics, University of Hull, Hull, HU6 7RX, UK
This paper compares the use of different lasers for the removal of Chlorinated Rubber (CR) coatings from concrete surfaces. The work involves the investigation of basic phenomena and reactions of CR to various laser wavelengths, including CO₂ (10.6µm), diode (810nm) and ArF excimer (193nm) laser radiation. Characteristics of beam absorption, residues and the thermal effects on the materials are analysed by optical microscopy, SEM, XRD, EDAX, etc.
The effects of different practical substrate materials, such as concrete and clay tiles have been investigated. The applicability of the different systems for the removal of CR paint contaminated with lead or radionuclides has also been studied.
- G-II/P15** GROWTH OF MICROCRYSTALLINE β-SiC FILMS ON SILICON BY ECR PLASMA CVD, S.J. Toal, H.S. Reehal, South Bank University, SEEIE, 103 Borough Road, London SE1 0AA, UK; N.P. Barradas, C. Jeynes, University of Surrey, Guildford, GU2 5XH, UK
We have investigated the growth of microcrystalline β-SiC films grown by ECR plasma CVD for application as a solar cell window material. The main reactant gases used were silane and methane. Hydrogen has been employed as the plasma gas with phosphine as the dopant gas. Film growth and properties have been investigated over a wide range of process parameters. This paper presents results on the structural and compositional properties of the films as a function of these process parameters, particularly growth temperature, ECR microwave power and reactant gas composition. The primary analysis techniques employed have been Rutherford Backscattering using the Simulated Annealing algorithm, and X-ray diffractometry.
We have found the grain size in our films to be limited to values less than 10nm. Both growth rate and crystallite size increase with sample temperature. In addition the growth rate increases with power while crystallite size reaches a maximum between 700 and 800 W. Small amounts of argon added to the reactant gases have a significant effect on the deposition kinetics and have produced the largest grain size in our material. An analysis of these findings is presented.
- G-II/P16** ENHANCEMENT OF DIAMOND NUCLEATION ON SILICON SUBSTRATES IN PULSED LASER ASSISTED HOT FILAMENT CVD, R. Schliesing, H. Zacharias, Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany; Q. Wang, V. Buck, Fachbereich Physik, Universität-GH Essen, Universitätsstraße 3, 45117 Essen, Germany
Diamond nucleation on untreated silicon substrates has been enhanced by pulsed laser radiation (λ= 532 nm) in a hot filament chemical vapour deposition reactor. Previous attempts employing ultraviolet or infrared irradiation showed that laser light at these wavelengths suppresses the diamond nucleation [1]. In the present study the effect of laser intensity on the diamond nucleation density is investigated. With laser irradiation up to 311 kW/cm² the diamond nucleation is enhanced by a factor 7, and taking the dwell time of the laser into account an enhancement by a factor of 5·10⁴ is observed. The reason for this may be the interaction between the light and the gas phase (excitation of molecular vibrations) and/or between the light and the surface (local heating, electronic excitation in the surface). The temporal distribution and maximum value of the surface temperature rise for a triangular laser pulse shape are calculated to investigate the influence of pyrolysis on laser enhanced diamond nucleation, which, however, is found to be not significant.
First applications to copper reveals also for this metal substrate a large enhancement of the nucleation rate. These observations, may lead to a growth of diamond layers at low substrate temperatures. Furthermore it may be possible to grow nanostructured diamond films.
[1] P.W. Morrison Jr., J.T. Glass in 'Properties and Growth of Diamond', ed. by G. Davis, INSPEC, the Institution of Electrical Engineers, London, 1994, p. 392.
- G-II/P17** EXCIMER LASER-INDUCED MODIFICATION IN PMMA / Ni-ACETYLACETONATE FILMS FOR SELECTIVE METALLIZATION, A. Jadin, K. Kolev and L.D. Laude, Laboratoire de Physique de l'Etat Solide, Université de Mons-Hainaut, 7000 Mons, Belgium
In the last few years, several excimer laser processing techniques for selective metal plating have been developed. Among these, the use of organometallic compounds, especially as precursors for metal deposition has proved to be a good approach. In this paper, a new specific application of organometallics for the generation of conducting patterns on flexible plastic substrates is presented. It consists in excimer laser irradiation of organometallic compounds (Ni-acetylacetonate) embedded in a polymer matrix of polymethylmethacrylate (PMMA). This laser processing induces photodecomposition of the organic compound which liberates metallic atoms in the polymeric medium. Further, electroless copper, nickel and gold plating was used for enhancement of the selective laser-induced nickel pattern. Results concerning the modifications of the medium upon excimer laser irradiation as well as the morphology of the metal films are reported.

SYMPOSIUM G

- G-II/P18** DYNAMICS OF LASER PULSE-INDUCED MELTS IN Ni-P VISUALIZED BY HIGH-SPEED TRANSMISSION ELECTRON MICROSCOPY, T. Nink, Z. Mao, O. Bostanjoglo, Optisches Institut, TU Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany
A current focus of interest concerning laser patterning of surfaces lies on amorphous Ni-P alloys. Due to [1] and [2] laser textured Ni-P layers can be used as cover layers for high performance magnetic disks. This is because laserpulses produce dome-like protrusions ("bumps") on the surface, which act as smooth support points for the contacting slider and provide low start/stop stiction and good durability [1]. This work presents the first time-resolved investigation of the development of these "bumps" in thin amorphous Ni-P films by means of high-speed transmission electron microscopy. The flow of the laserinduced melt, the pile-up of the "bump" and the solidification were examined with a space/time resolution of 1 μm and down to 10 ns. First high-speed pictures of these processes were obtained and will be presented.
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This work was supported by the A.v.Humboldt Foundation and the Deutsche Forschungsgemeinschaft (DFG)
- G-II/P19** VUV LASER ABLATION OF POLYMERS AT 157 NM AND APPLICATIONS FOR 3D PROCESSING, M. Lapczyny, M. Stuke, MPI f. biophys. Chemie, P.O. Box 2841, 37018 Göttingen, Germany
- G-II/P20** FOCUSED ION BEAM INDUCED NANOSCALE MODIFICATION OF 3D MICROSTRUCTURES, A. Schertel*, R. Kassing**, M. Stuke, Max-Planck-Institut f. biophys. Chemie, P.O. Box 2841, 27018 Göttingen, *Micrion, **Univ. Kassel, Germany
- G-II/P21** RELATIVISTIC MAXWELLIAN ELECTRONS EMITTED AFTER SURFACE IRRADIATION WITH ULTRA SHORT LASER PULSES, J. Marciak-Rozlowaka, Institute of Electron Technology, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
The implementation of the chirped pulse amplification (CPA) systems onto high power lasers has made available new intensity regimes that were previously inaccessible in the laboratory. At intensities of 10^{18} Wcm^{-2} the electron oscillatory velocity for 1 μm radiation becomes relativistic and the radiation pressure reaches 300 Mbar. Interesting, new physical phenomena have been predicted in this regime such as emission high energetic electrons, ions and MeV x-ray.
In this paper the relativistic distribution function for particle velocity is discussed. Assuming the local thermalization of relativistic electron the velocity spectra for electrons will be obtained. It will be shown that for temperatures $T \approx m_e$ the spectra are localized in the vicinity of the particle velocities $u \approx c$. The shape of the spectra is mostly described by the term γ^2 where $\gamma = (1 - (u^2/c^2))^{-1/2}$.
- G-II/P22** THE USE OF LIQUID PRECURSORS IN PLASMACHEMICAL TECHNOLOGY OF OBTAINING a-SiC:H THIN FILMS, L. Ivashchenko, G. Rusakov, V. Ivashchenko, Institute of Problems of Material Sciences, Ukraine NAS, Dep.4., Krzhyzhanovsky Str.3, 252680 Kyiv, Ukraine
The analysis of experimental data has shown promise of our technological approach in obtaining amorphous silicon carbide films. The amorphous hydrogenated silicon carbide films received by a plasmachemical decomposition of CH_4 , SiCl_4 steams, delivered in the chamber by a stream of hydrogen, in the plasma of RF- discharge. On a substrate the negative potential are supplied. For obtaining n-conductivity in a gas mixture the nitrogen was added. For p-conductivity the BCl_3 steams were entered which was decomposed in the plasma. Substrates were glass, monocrystalline silicon. The influence of parameters of a deposition on composition, structure, morphology and physical properties of obtained films are investigated. It is established, that in depositing films on a conducting substrate (monocrystalline silicon) the maximum magnitude of $\mu \cdot n$, is about $3 \cdot 10^{17} (\text{cm}^2 \cdot \text{V})^{-1}$ for $U_d = -200\text{V}$ and decreases on three order in decreasing U_d up to 0 or increasing up to -600V .
On base of the theoretical calculations of a-SiC by the recursion method of Haydock it is suggested the mechanism of an influence of amorphousation and hydrogenation on the electronic structure of the silicon carbide that is necessary for understanding the physics of the process of doping, hydrogenation of amorphous thin films and will allow to obtain the a-SiC:H films with the necessary properties.
- G-II/P23** ELLIPSOMETRIC STUDIES OF RAPIDLY-QUENCHED Fe-Cr-B RIBBONS SUBJECTED TO LASER TREATMENT, M. Zakharenko, I. Yurglevych, L. Poperenko, Taras Shevchenko University, 64 Volodymyrska st., 252033 Kyiv, Ukraine
The as-quenched and laser treated $(\text{Fe}_{0.9}\text{Cr}_{0.1})_{85}\text{B}_{15}$ ribbons were studied by ellipsometric method. The laser treatment of the sample surface was performed by the pulse YAG-laser ($\lambda = 1.06 \mu\text{m}$). The angular dependences of ellipsometric parameters such as a phase shift between the orthogonal components of the polarization vector Δ and an azimuth of the restored linear polarization Ψ were obtained using the null ellipsometric method by means of the LEF-3M-1 ellipsometer with operating wavelength $\lambda = 632.8 \text{ nm}$. The values of the principal angle of incidence ϕ_p were calculated from these dependences.
 ϕ_p at fixed pulse energy E was found to depend on quantity of laser pulses N nonmonotonously reaching the minimum at the certain N, that depends on E. The similar changes ϕ_p of on E were observed, N being fixed. Such behaviour of ϕ_p as well as optical conductivity σ is thought to be caused by the effect of laser glazing of the surface which consists in the additional disordering of subsurface layers of the ribbons, containing some amount of crystalline inclusions. When large enough radiation dose is reached, the annealing of the surface may be observed, the crystalline phases being formed. This, in turn, leads to ϕ_p enhancement, that we observed experimentally for high values of N and E.
- G-II/P24** OPTICAL CHARACTERIZATION OF THE PLASMA PROCESSED METALLIC SURFACES, L.V. Poperenko, M.V. Vinnichenko, Taras Shevchenko Univ., prosp. Glushkov 6, 252022 Kyiv, Ukraine; A. Roeseler, ISAS - LSMU, Rudower Chaussee 5, 12489 Berlin, Germany
The main purpose of the work is to clarify the nature of the metallic surface modification by high-dose ion implantation. The samples of Mo, Al, Ta implanted by copper ions as well as of Mo and Ti implanted by mixed Ti^+ and C^+ beam were probed by means of the infrared Fourier transform spectroellipsometry. Spectral dependencies of the refraction and absorption indices, dielectric function (DF) and optical conductivity (OC) were then calculated for the wavelength range 2-25 μm . It has been observed essentially different spectral behavior of the optical parameters for metallic surfaces modified by copper ions in comparison with those modified by mixed Ti^+ and C^+ beam. The latter showed typical for unmodified metals Drude-like behavior of the OC and DF. Modification of Al, Mo and Ta by copper ions leads to entirely different from the Drude-like behavior of the optical properties that could be described in terms of the Kaveh-Mott equation.

- G-II/P25** **DEPOSITION OF NANOPHASE Cr_2O_3 UNDER LASER IRRADIATION OF SOLID-LIQUID INTERFACE**, S.I. Dolgaev, N.A. Kirichenko, and G.A. Shafeev, General Physics Institute, Russian Academy of Sciences, 38 Vavilov street, Moscow 117942, Russia
The deposition of epitaxial films of Cr_2O_3 , Fe_2O_3 , and MnO_2 under laser irradiation of the interface sapphire-absorbing liquid has been reported recently. In similar experimental conditions, laser irradiation of the interface amorphous solid-liquid results in deposition of a polycrystalline film. In the present paper, the deposition of Cr_2O_3 on a glass substrate induced by radiation of a copper vapor laser is studied. Irradiation of the interface glass-aqueous solution of CrO_3 at fluence of $2\text{--}5 \text{ J/cm}^2$ at $\lambda = 510.6 \text{ nm}$ results in the deposition of Cr_2O_3 which consists of oriented nanoclusters with size of $8\text{--}20 \text{ nm}$. The subsequent chemical etching of the glass results in a free-standing film of nanophase Cr_2O_3 with lateral dimensions of several mm^2 and $30\text{--}50 \text{ nm}$ thick. The mathematical model of the deposition process is considered based on the semi-analytical solution of the non-stationary heat diffusion equation for a gaussian profile of laser beam. It is shown that during a ns laser pulse the maximum of the temperature shifts from the interface towards the absorbing liquid. The results of calculations are qualitatively consistent with experimental data on the dependence of the thickness of Cr_2O_3 deposit on the heat diffusion coefficient of a solid substrate.
- G-II/P26** **ELECTROLESS Cu DEPOSITION ON LASER-ABLATED POLYIMIDE SURFACE**, G.A. Shafeev, E.N. Loubnin*, and P. Hoffmann**, General Physics Institute, Russian Academy of Sciences, 38 Vavilov street, Moscow 117942, Russia; *Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, Moscow 117915, Russia; **Swiss Federal Institute of Technology, Department of Microtechnique, Institute of Applied Optics, Lausanne 1015, Switzerland
Laser ablation of polyimide surface results in the formation of a glassy carbon layer on its surface, especially at near-threshold fluence [1]. Glassy carbon can mediate the electroless metal deposition resulting thus in a local metallization of the surface, as it has been shown recently for the ablated surfaces of polyimide (cw argon ion laser, [2]) and diamond [3]. In the present work, this carbon layer is produced by ablation of polyimide in air by either a copper vapor laser (wavelength of 510.6 nm) or by an excimer KrF laser (wavelength of 248 nm). The ability of this layer to promote the electroless Cu deposition from the corresponding plating solution is studied as the function of laser processing parameters and conditions of deposition. The early stages of metal deposition are analysed by XPS technique. The effect of exposure of the glassy carbon layer to visible radiation on the rate of deposition is studied. The possible mechanisms of the electroless deposition on the glassy carbon are discussed.
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- G-II/P27** **LASER WRITING OF GLASSY CARBON FEATURES ON Si FROM LIQUID TOLUENE**, G.A. Shafeev, A.V. Simakin, A.A. Lyalin, E.D. Obraztsova, and V.D. Frolov, General Physics Institute of the Russian Academy of Sciences, 38 Vavilov street, 117942 Moscow, Russia
Laser-assisted deposition from liquid phase is characterized by a high density of precursors (up to 10^{20} cm^{-3}) and high deposition rates. The decomposition of the precursor by a ns laser pulse results not only in the deposition on the irradiated areas of substrate but also in the formation of a dense suspension of clusters of the deposited material in the bulk of precursor solution. These clusters take part in the nucleation and growth of the deposited material inside the exposed areas of the substrate. In the present paper, a copper vapor laser (wavelength of 510.6 nm , pulse duration of 20 ns , repetition rate of 8 kHz) is used to deposit the μm carbon features on a Si substrate immersed in liquid toluene. The carbon deposit is well adherent to Si substrate and forms the ohmic contact. Raman analysis show that the deposit consists of glassy carbon with particle size of $4\text{--}5 \text{ nm}$. The cold emission of electrons from the deposited features is studied as the function of experimental parameters. Mapping the work function of the carbon deposit with a scanning tunnel field emission microscope (STFEM) shows that the maximum of work function correspond to the boundaries of larger grains of $20\text{--}30 \text{ nm}$ in size. The emission characteristics of the carbon deposit are modified by addition of organometallic precursors of Au or Pt to toluene which results in doping of the deposited carbon with corresponding metal nanoclusters. The topology of the carbon deposit is discussed in view of competition between the processes of heterogeneous decomposition and laser-assisted coagulation of carbon clusters produced in the bulk of liquid.
- G-II/P28** **FILMS OF HgCdTe FORMED ON TWO KINDS OF Si SURFACES**, M. Kuzma, G. Wiesz, E. Sheregii, Institute of Physics, Higher Pedagogical School, Rejtana 16a, 35-309 Rzeszow, Poland; T.Ya. Gorbach, P.S. Smertenko, S.V. Svechnikov, Institute of Semiconductor Physics, National Ukrainian Academy of Sciences, Prospect Nauki 45, Kiev 28, 252630 Ukraine
Films of CdHgTe have been obtained by laser ablation method in dynamic vacuum ($p \sim 10^{-6} \text{ Torr}$). Two various kinds of Si-surface were used as substrate: a) flat surface polished and chemically etched and b) anisotropically chemically etched. It is known that this two surfaces have different crystallographic and physical properties. Morphology of films of various thickness, their structure and composition have been studied. Microscopic investigations point out the considerable difference of a thickness of Si- HgCdTe interlayer. Properties of two longitudinal and vertical electrical conductivity as well as C-V characteristics were studied for both cases.
- G-II/P29** **EMPLOYMENT OF A SELECTIVE ETCHING METHOD TO CORRECT TECHNOLOGICAL PROCESSES**, T.F. Rusak, K.L. Enisherlova, SRI „Pulsar“, Moscow, Russia and G.N. Petrov, T.M. Tkacheva, „Ellina-NT“, Moscow, Russia
Peculiarities of defect formation in subsurface layers of silicon wafers under heat treatments are determined, beside the temperature and surface treatment peculiarities, by the properties of the wafer material ($\text{N}[\text{oi}]$, $\text{N}[\text{Cs}]$, ΔSi , ΔV) and by the influence of an environment in which the heat treatment is carried out. Having a certain experience in separating the influence of these factors, one can voice a number of suppositions about the defect formation in the wafer bulk (precipitation for intrinsic gettering, appearance of dislocation loops which can spread into device regions etc.) by using, results of surface defect investigation. Methods of selective etching which are distinguished by their simplicity and clearness can be used for these aims. But these methods need a further improvement. To develop the modernization methods of selective etching, silicon wafer surfaces after ion implantation with carbon and oxygen and heat treatments, analogous to those in the device manufacturing, were used. The analysis, performed by SEM on the obtained etched figures has permitted increase in information and reliability of the developed methods of selective etching. The developed methods has been tested when the intrinsic gettering regimes are being improved. The testing included the analysis of etching figures after the 1-st oxidation and the correction of further steps of the gettering centers formation by taking into account the material peculiarities.
- G-II/P30** **THE USE OF LIQUID PRECURSORS IN PLASMACHEMICAL TECHNOLOGY OF OBTAINING a-SiC:H THIN FILMS**, L. Ivashchenko, G. Rusakov, V. Ivashchenko, Institute of Problems of Material Sciences, Ukraine NAS, Dep.4. 252680 Kyiv, Krzhizhansky Str.3, Ukraine
The analysis of experimental data has shown promise of our technological approach in obtaining amorphous silicon carbide films. The amorphous hydrogenated silicon carbide films received by a plasmachemical decomposition of CH_3SiCl_3 steams, delivered in the chamber by a stream of hydrogen, in the plasma of RF-discharge. On a substrate the negative potential are supplied. For obtaining n-conductivity in a gas mixture the nitrogen was added. For p-conductivity the BCl_3 steams were entered which was decomposed in the plasma. Substrates were glass, monocrystalline silicon. The influence of parameters of a deposition on composition, structure, morphology and physical properties of obtained films are investigated. It is established, that in depositing films on a conducting substrate (monocrystalline silicon) the maximum magnitude of m-no is about $3\text{--}10^{17} (\text{cm}^{-2}\text{--V})^{-1}$ for $\text{Ud} = -200 \text{ V}$ and decreases on three order in decreasing Ud up to 0 or increasing up to -600 V . On base of the theoretical calculations of a-SiC by the recursion method of Haydock it is suggested the mechanism of a influence of amorphousation and hydrogenation on the electronic structure of the silicon carbide that is necessary for understanding the physics of the process of doping, hydrogenation of amorphous thin films and will allow to obtain the a-SiC:H films with the necessary properties.

- G-II/P31** **LASER IMPLANTATION OF MOLECULAR AGGREGATES INTO POLY (METHYL METHACRYLATE),** M. Goto, N. Ichinose, S. Kawanishi, Japan Atomic Energy Research Institute, 25-1, Mii-Minami-Machi, Neyagawa, Osaka 572, Japan and H. Fukumura, Osaka University, Suita, Osaka 565, Japan
Novel electronic and optical devices fabricated with organic molecules have recently attracted much attention. One of the methods to manufacture those devices is to implant molecules in a solid polymer with pulsed laser irradiation. For performing the laser implantation of molecules, it is necessary to prepare a source polymer film containing organic molecules, meaning that a common solvent for the polymer and the molecules is required. Here we report a new technique to implant molecular aggregates by laser irradiation without using any solvents. Polymer tablets were prepared by compressing organic molecular microcrystalline and polymer powder as implantation sources. The tablets were overlaid on a polymer target and irradiated with laser pulses. After the irradiation, absorption and fluorescence spectra of the target showed that molecules remain intact and form aggregates in the target film. Surface analyses by atomic force microscopy revealed that the first laser pulse deposited molecular aggregates at the target surface and further irradiation let them diffuse into the target polymer. On the basis of the experimental results the implantation mechanism will be discussed.
- G-II/P32** **PHASE COMPOSITION OF CR-C THIN FILMS DEPOSITED BY DOUBLE UNBALANCED MAGNETRON SPUTTERING SYSTEM,** S. Groudeva-Zotova, IE-BAS, Tzarigradsko Chausse 72, 1784 Sofia, Bulgaria, R. Vitchev and J. Helsen, Universiteit Leuven, 3001 Leuven, Belgium
PVD thin films of the system Cr-C are among the materials of interest for hard, wear-resistant and corrosion-resistant coatings. However the properties and the stability of such coatings depend strongly on the film structure and phase composition. Nonreactive dc magnetron sputtering by 2 unbalanced magnetron sources was used for deposition of Cr-C films with C:Cr ratio in the range 0.8-2.04. The phase composition of the films is investigated by X-ray diffraction, XPS-analysis, SEM and resistivity measurements. The combination of these methods allows to find some differences in the phase composition of films with similar XRD patterns and to distinguish 4 main phase composition areas in the investigated compositional range: 1/ Microcrystalline films containing both supersaturated Cr-C solution and the low-C stoichiometric carbide phase β ; 2/ Microcrystalline films dominated by the β phase; 3/ Amorphous-like films containing different carbides and 4/ Amorphous films consisting of amorphous carbon matrix and few low-Cr carbide microcrystals dispersed in it.
- G-II/P33** **THERMAL BEHAVIOUR OF Co/Si/W/Si MULTILAYERS UNDER HIGH INTENSITY EXCIMER LASER PULSES,** E. Majkova, S. Luby, M. Jergel, Slovak Acad. Sci., 8342 28 Bratislava Slovak Republic, A. Luches and M. Martino, University of Lecce, 73100 Lecce, Italy, P. Mengucci, G. Majni, University of Ancona, Italy
The thermal stability of e-beam deposited multilayers (MLs) for soft X-ray reflection optics was studied under XeCl laser processing in vacuum. MLs with five Co/Si/W/Si periods, each 13.5 nm (MLS1) or 18.4 nm (MLS2) were deposited onto oxidized Si and irradiated at the fluences 0.075-0.6 Jcm⁻² by 1 or 100 pulses. The samples were analyzed by X-ray diffraction, hard X-ray reflectivity and sheet resistance measurements. In MLS1 the Co films were discontinuous, in MLS2 they were continuous. The layered structure of our samples persists up to 0.6 Jcm⁻², 1 pulse for MLS2 and 0.6 Jcm⁻² 100 pulses for MLS1 irradiations. The thermal stability of MLS1 is even better than for W/Si MLs measured previously. In laser irradiated samples Co₂Si₃ phase prepared normally only under high pressures (>4GPa) was found. It was not reported in the film couples so far. The high thermal stability and Co₂Si₃ formation in MLS1 are explained by complex Co-Si silicide formation conditions and compressive stress parallel to the surface of irradiated samples, respectively.
- G-II/P34** **EXITED GAS-INDUCED CVD OF DIELECTRIC FILMS FROM MOLECULAR PRECURSORS,** T.P. Smirnova, L.V. Yakovkina, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Dpt., Lavrentjev Ave 3, Novosibirsk, Russia
As a starting substances for dielectric films deposition we have used hexamethyldisilazane, hexamethylcyclotrisilazane, trimethylchlorosilane and borazine for the silicon oxide, silicon nitride, silicon carbide and boron nitride films deposition respectively. As opposed to conventional plasma enhanced process the exited gas-induced remote plasma CVD process made it possible to safe "ready-made" fragments of starting molecule as the process is performed. A relations between deposition conditions, chemical composition, optical and structural properties were explored using IR- spectroscopy, ellipsometry and diffractometry of synchrotronous radiation. Electron spin resonance was used for detection of dangling bonds in film. If passed through a plasma region gases were able to store high energy, for example helium, deep dehydrogenation of borazine and full bearing away of organic radicals from silazanes are observed under interaction of these gases with monomers. Because of using molecular precursors and plasma exited gases, which stored high energy, the high-quality films were obtained.
- G-II/P35** **SYNTHESIS OF OXIDE-CERAMIC AT MAGNESIUM AND ZIRCONIUM ALLOYS,** H.M. Nykyforchyn, M.D. Klapkiv, V.M. Posuvaylo, Karpenko Physico-Mechanical Institute of NAS of Ukraine, 5 Naukova St., 290601 Lviv, Ukraine
The surface oxidation technology of magnesium and zirconium alloys in electrolyte plasma has been created. When the voltage of some hundreds of volts is subjected to a metal-electrolyte system, electric discharges of intensity of nearly 10⁷ V/m occur. It results in plasma appearance in the discharge channels. The density of plasma electrons ($n_e \approx 10^{22} \text{m}^{-3}$) was determined by spectrum- line broadening of H α due to the Stark effect. The plasma electron temperature ($T_e \approx 10^4 \text{K}$) was determined by relative intensity lines of metals atoms and ions. The dependencies of amounts of yields of reactions of these metals with oxygen are calculated. Using of the optimum volt-ampere parameter and electrolyte content allows to obtain at the magnesium and zirconium alloys oxide-ceramic coatings thickness 50-250 μm and microhardness 10 GPa.
- G-II/P36** **LASER INDUCED DEFORMATION ON HARD DISK SURFACE,** D.M. Liu, Y.F. Lu, W.J. Wang, K.T. Chang, R.J.K. Goh and T.S. Low, Laser Research (Singapore) Pte Ltd and Data Storage Institute, 10 Kent Ridge Crescent Singapore, 119260
Laser induced deformation on hard disk surface has been observed. A diode pumped Q-switched vanadate laser with wavelength of 1064 nm and TEM₀₀ mode is used in this experiment. The laser pulse duration is in the range of 30 ns to 100 ns. The laser pulse energies around several μJ are used. The sample is a commercial hard disk on which NiP sublayer, chrome underlayer, magnetic coating, carbon overcoat and lubricant are coated subsequently. AFM is used to analyze the change of surface morphology. The deformed surface looks like flower-shaped wrinkle with a center circular protrusion or stripe-shaped wrinkle which depends on the laser fluence used. Evaporated material analysis, surface wear test and surface structure analysis are performed to understand the mechanism of surface deformation. Since there are strong internal stresses in the multi-layer hard coating, the surface deformation is possibly due to internal stress release during surface melting induced by laser irradiation.

- G-II/P37** EFFECTS OF SURFACE OXIDE DENSIFICATION ON RIPPLE GROWTH IN EXCIMER LASER IRRADIATED SILICON SUBSTRATES, Y.F. Lu and J.J. Yu, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Laser-induced ripple structures in silicon substrates covered with rapid-thermal-annealed radio-frequency-sputtered silicon dioxide films have been investigated using KrF excimer laser irradiation for controlling the periodicity. It was found that rapid thermal annealing (RTA) of the oxide film could not change the topography of ripple structure but enhance the ripple growth. This can be predicted by our model in terms of the RTA-induced densification of oxide films, which means that the surface oxide can control the ripple growth by its density in addition to its layer thickness. The ellipsometric measurements indicated that RTA processing of the oxide film gave rise to an increase in its refractive index, and hence, its density. Furthermore, increasing either the annealing temperature or the annealing time can enhance the ripple growth. However, increasing annealing time may be more efficient for ripple enhancement. In addition, our experimental results showed no conceivable influence of the SiO₂/Si interface layer on the ripple growth. This study provided insight into the understanding of surface oxides in controlling the ripple pattern induced in substrates, which will be beneficial in producing required ripple structures for laser microtexturing or solar cell fabrication.

- G-II/P38** LASER-INDUCED RIPPLE STRUCTURES ON Ni-P SUBSTRATES, J.J. Yu and Y.F. Lu, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

The laser-induced ripple structures in NiP disks are experimentally investigated by varying laser fluence and pulse number. A quantity $[R_s / (\lambda/2)]$ is proposed to characterize the real contact area at the head-disk interface. This quantity is defined as the ratio of roughness height R_s to half ripple period $(\lambda/2)$. The maximum shear stress and the plasticity index have been derived to analyze the ability for ripple structures to withstand stress and the head-ripple contact mode, respectively. Increasing fluence and pulse number may lead to an increase in ripple periodicity, and on the contrary, decreases in corresponding maximum shear stress, real contact area $[R_s / (\lambda/2)]$ and plasticity index. The laser parameters (fluence and pulse number) represent effective approaches to improve the tribology of the head-disk interface by controlling the laser-induced ripple pattern such as periodicity and roughness height. The laser irradiation with lower fluence and fewer pulses is helpful in producing the required ripple structure for laser texturing in magnetic media. This structure can meet the requirements of elastic contacts between head and disk, and less deformation under stress while without pronounced sacrifice in contact-area reduction.

- G-II/P39** FAST ICCD IMAGING OF KRF EXCIMER LASER INDUCED Ti PLASMA PLUMES FOR Si METALLIZATION, M.H. Hong, Y.F. Lu, T.M. Ho, L.W. Lu and T.S. Low, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent Singapore 119260

The dynamics of plasma plumes induced by KrF excimer laser irradiation on Ti target for pulsed laser deposition of Ti thin film on Si substrate is investigated by fast ICCD time-integrated photography. Side view of the plasma plumes at different time after the laser ablation of the target is taken to study the evolution of the plasma plume inside the PLD chamber and its interaction with the substrate. Dynamics of the front view of the plume is also captured to get more information on the Ti thin film distribution on the substrate. Plume flying and expansion velocities in the directions normal and parallel to the target surface are calculated. The fast ICCD images show that the plume starts to fly and expand at velocities as high as 10⁴ m/s during the first microsecond after the laser ablation and reduces gradually to zero with the increasing delay time. The dependence of the plume size, flying and expansion velocities on laser fluence, delay time, distance between target and substrate, and the pressure inside the vacuum chamber is analyzed to optimize the parameters for laser deposition of Ti thin film on Si substrates.

- G-II/P40** MINIMUM SIZES OF PARTICLES REMOVED BY LASER IRRADIATION, W.D. Song and Y.F. Lu, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

A cleaning model for laser removal of particles from solid surfaces has been developed. The Van der Waals force and cleaning forces have been taken into account. If the cleaning force exceeds the adhesion force, the particle may be detached from the substrate surface. The minimum sizes of particles removed by laser irradiation r_{th} is given as $r_{th}^{1/3} = h Z / (8 \pi^2 Z^3 \gamma E \Delta T (0, t) - h) [(3h / 3 2 \pi Z^2) (1 - \nu^2 / E)]^{2/3}$ where h , z , γ , E , ΔT and ν are the material-dependent Lifshitz-Van der Waals constant, the atomic separation between the particle and substrate surface, the thermal expansion coefficient, the Young's modulus, the temperature rise at the substrate surface and Poisson ratio of the substrate, respectively. In order to verify the above theoretical predictions, the following experiments have been carried out. Alumina and quartz particles with different sizes were chosen as particulate contaminants on single crystal silicon surfaces in our experiments. The minimum size of particles obtained from the experiments is in good agreement with the theoretical curves.

- G-II/P41** STUDY OF PULSED-LASER-INDUCED ALUMINUM PLASMA SPECTRA, Y.F. Lu, Z.B. Tao, M.H. Hong, D.S.H. Chan and T.S. Low, Laser Microprocessing Lab, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Emission spectrum of aluminum plasma induced by 1064 nm pulsed Nd:YAG laser is investigated by an Optical Multichannel Analyzer (OMA). Spectroscopic study shows that aluminum spectrum becomes relatively abundant with increasing incident laser fluence. Al, Al⁺, Al⁺⁺ spectral lines are observed successively with high laser fluence. The emission of plasma radiation is analyzed to explain the plasma spectra. The threshold for the laser ablation with Al is about 0.7 J/cm². The appearance of excited Al, Al⁺, Al⁺⁺ spectral lines are about 0.7, 0.8 and 1.0 J/cm² respectively. Plasma density is estimated from the profiles of Al⁺ (358.7nm) spectral line with different gated time and incident laser fluences. Plasma temperature is also estimated from relative intensities of two different spectral lines.

- G-II/P42** DEPOSITION OF BORON-CARBON-NITROGEN THIN FILMS BY ION-BEAM-ASSISTED EXCIMER ABLATION OF GRAPHITE, Z.M. Ren, Y.F. Lu, H.Q. Ni, D.S.H. Chan, and T.S. Low, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Boron-Carbon-Nitrogen B₃C₂N₂ thin films were deposited by excimer ablation of boron carbide (B₄C) under nitrogen ion-beam bombardment. The electronic and compositional properties of the deposited thin films were analyzed by X-ray photoelectron spectroscopy (XPS), Fourier Transform Infra-red (FTIR) and Raman measurements. The results showed that carbon, nitrogen and boron species were chemically bonded to each other instead of simple mixing. Detailed analyses showed that the ion-beam bombardment can lead to breaking of B-C bonds and formation of C-N and B-N bonds. Different compositional ratio of x:y:z can be realized by adjusting the excimer and the ion-beam parameters. An appropriate ion-beam energy (probably less than 1 keV) was proposed for the purpose of the synthesis of the boron-carbon-nitrogen thin films. The optical properties of the as-deposited thin films were characterized by Ellipsometry measurement.

G-II/P43 CARBON NITRIDE THIN FILMS DEPOSITED BY KrF EXCIMER ABLATION OF GRAPHITE IN NITROGEN ATMOSPHERE, Z.M. Ren, Y.F. Lu, H.Q. Ni, D.S.H. Chan and T.S. Low, Laser Microprocessing Laboratory, Department of Electrical Engineering and Data Storage Institute, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Carbon nitride thin films were deposited on silicon wafers by pulsed KrF Excimer (wavelength 248 nm, duration 23 ns) ablation of graphite in nitrogen atmosphere. Different excimer fluences and pressures of the nitrogen atmosphere were used in order to achieve a high nitrogen content in the deposited thin films. Fourier Transform Infra-red (FTIR) and X-ray photoelectron spectroscopes (XPS) were used to identify the binding structure and the content of the nitrogen species in the deposited thin films. The highest N/C ratio 0.42 was achieved at the excimer fluence of 0-8 Jcm⁻² at a repetition rate of 10 Hz with the pressure of the nitrogen atmosphere P_N=100 mTorr. A high content of C=N double bond instead of C≡N triple band was indicated in the deposited thin films. Ellipsometry was used to analyze the optical properties of the deposited thin films. The carbon nitride thin films have amorphous-semiconductor-like characteristics with the optical band gap E_{opt} as high as 0.42 eV. The influence of the substrate temperature on the electronic properties of the deposited thin films was studied by Raman spectroscopy.

Thursday June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-Midi

Poster Session III
17:30-19:00

- G-III/P1** FEMTOSECOND AND NANOSECOND PULSE-LASER MATERIAL PROCESSING IMAGED BY TIME RESOLVED PHOTOELECTRON MICROSCOPY, M. Weingärtner, R. Elschner, O. Bostanjoglo, Optisches Institut, TU-Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany
The fundamental processes of laser solid interactions are completely different for nanosecond resp. femtosecond laser pulse material treatment. Because of the extremely high power densities of fs-laser pulses and the short energy deposition time the classical theory of energy flow in the material is no longer valid. A two temperature model for electrons and lattice has to be used, and material modification like evaporation and plastic deformation is possible without thermal melting.
Using a high speed photoelectron microscope with a time resolution of 5 ns the transient stages of laser processing of Si and Co were investigated. With ns laser pulses the expected thermodynamical and chemical processes take place, like melting and crystallisation, removal or enhancement of adsorbate and oxide layers. In contrast, applying fs laser pulses, athermal evaporation of silicon is observed, resulting in sharply edged pits with a flat ground. This effect only takes place with energies above a sharp threshold which depends on whether a native oxide layer is covering the surface or not. Treating a polycrystalline cobalt foil produces within some ten ns elastic and plastic deformations and movement of grain boundaries.
This work was supported by the Deutsche Forschungsgemeinschaft.
- G-III/P2** ION BEAM ANALYSIS OF PULSED LASER DEPOSITED Ti: SAPPHIRE, P.H. Key and M.J.J. Schmidt*, Department of Applied Physics, The University of Hull, Hull, HU6 7RX, UK; * now at: Manufacturing Division, Department of Mechanical Engineering, University of Manchester Institute of Science and Technology (UMIST), PO Box 88, Manchester, M60 1QD, UK
Pulsed laser deposition (PLD) has been established as a growth method for thin films of optically active materials such as Ti:Sapphire and Nd:YAG,
In this paper we describe the ion beam analyses of Ti:sapphire films deposited by PLD onto single crystal Si and MgO substrates at 300, 900 and 1400 K. Rutherford back-scattering (RBS) and Proton induced x-ray emission (PIXE) results are reported and interpreted in correlation with x-ray diffraction (XRD) analysis.
The highest quality films we have grown are shown to consist of polycrystals of Ti doped α -Al₂O₃, in mainly two orientations. The PIXE investigations indicate a reduction in the Ti ion dopant concentration in the films when compared to the bulk source material, the loss presumably occurring during the transfer of material from ablation target to the substrate.
The influence of the deposition parameters on the resulting films are discussed.
- G-III/P3** STUDY OF THE DIFFERENT PULSED LASER HEATING REGIMS OF METALS, L. Vivet, J. Arnoult, T. Legrand, GREMI, Université d'Orléans/C.N.R.S., 45067 Orléans cedex 2, France
The laser has become over the past dozen years a familiar thermal processing tools for annealing, alloying, cutting, welding, drilling, heat treating of various materials. The laser energy density (F) and the interaction duration (τ_p) are the main parameters which allow to identify the different regimes of laser heating associated to the different thermodynamic modifications which determine the application domains. We have studied these different regimes of laser heating for various metals: Cu, Au, Ag, Pb, irradiated by the pulsed laser beam of a Nd:YAG laser. The numerical modeling of the laser heating and the resulting thermodynamic transformations of these metals have been achieved taking into account the temperature dependence of the thermodynamic and the optical properties. Four different regimes of laser heating have been distinguished by considering the evolution of the maximum melted depth (H_{melt}) the maximum vaporised depth (H_{vap}) and the maximum depth of the melted zone (δ H_{melt}) as a function of {F, τ_p }. For these calculations τ_p has been varied from tens of ns to tens of ms and F has been varied from tens to hundreds of J/cm². The results we obtained allowed to define, for each metal, the range of {F, τ_p } values for which the laser welding process, on a limited depth (from 10 to 100 μ m), can be achieved. These calculations also showed that in the strong laser vaporisation regime, the thermal diffusion depth δ th increases very quickly with F for a given value of τ_p , making the usual definition of δ th irrelevant for this particular regime, as observed in different experimental studies.
- G-III/P4** STUDY OF PARTICLES EJECTED AFTER PULSED LASER ABLATION OF A GRAPHITE TARGET, B. Angleraud, F. Garrelie, F. Tétard, A. Catherinot, LMCTS UPRESA CNRS n°6015, 123 av. A. Thomas, 87060 Limoges cedex, France
This work is devoted to the study of the μ m-sized particles ejected after pulsed laser ablation of a graphite target. The time evolution of these particles is investigated by fast imaging CCD. The influences of the laser fluence and of the background gas pressure on the particles motion are presented for laser fluence and pressure ranging 9 - 5000 J/cm² and 10⁻⁴ - 20, 10⁻³ Pa respectively.
The delay t between the beginning of the laser pulse (duration 20 ns) and the detection of the particles is of about 5 μ s. They are detected for delays up to several ms. Their velocity is ranging between few hundreds and two thousands ms for the laser fluence studied.
The influence of the number of laser pulses on the ejection of particles is also studied. The results are quite different according to the laser fluence value.
Image processing of optical photographs of various pulsed laser deposited carbon films have been performed to determine the size and the surface density of the particles deposited.
- G-III/P5** LASER-INDUCED DESORPTION OF VARIOUS TUNGSTEN OXIDES ON POLYCRYSTALLINE W SURFACES, Cs. Beleznai*, D. Vouagner*, J.P. Girardeau-Montaut* and L. Nanai**, *Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard - Lyon 1, 43, Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France; ** Department of Experimental Physics, Jozsef Attila University, 6720 Szeged, Dom t. 9., Hungary
In-situ monitoring of the vacuum chamber pressure during laser-induced oxide desorption on W surfaces provides a view on the desorption process. Sudden pressure variations suggest a change in the desorption kinetics. Numerical integration of the observed pressure evolution yields a relationship for the surface coverage function.
During the desorption experiment, due to the incident pulsed UV laser light, photoelectrons are ejected from the sample surface. Evaluating the temporal change in the measured charge shows a good agreement with the obtained pressure measurements.
These results are attributed to the specific oxide structure on the W consisting of various tungsten oxides.

SYMPOSIUM G

- G-III/P6** CHARACTERIZATION OF THE OXIDE REMOVAL KINETICS ON K⁺-IMPLANTED W SAMPLES, D. Vouagner*, Cs. Beleznai^{*,**} and J.P. Girardeau-Montaut*, *Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard - Lyon 1, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France; **also at the Department of Experimental Physics, Jozsef Attila University, 6720 Szeged, Dom t. 9., Hungary
K⁺-implanted W samples with various implantation depths were investigated. Generally, implantation of alkali ions gives rise to two competitive effects: it lowers the surface work function, however it enhances surface oxidation too which in turn leads to a slight work function increase. In opposite to alkali overlayers, implanted species confined within a 'metallic cage' resist to the applied laser irradiation and alkali removal occurs only to a small extent. Measurements of laser-induced photoelectric charge pulses indicate a variation of the photoemission yield as a function of surface oxide thickness. Moreover, following the charge pulse evolution over a longer period (2-3 hours), one finds that the laser-induced oxide removal characteristics depends on the implantation parameters as well. Results are compared to those obtained for pure, non-implanted W and mechanisms responsible for the work function lowering are discussed.
- G-III/P7** EXCIMER LASER ABLATION STUDIES OF TITANIUM, P. Clarke, P.H. Key and P.E. Dyer, Department of Physics, University of Hull, HU6 7RX, UK
Laser ablation-deposition is now a well established and versatile method for the preparation of thin films of elemental and complex compound materials.
Nitrides, carbides and oxides of titanium have applications in both electronics and as optical coatings.
Laser ablation of titanium in low pressure gaseous environments allows vapour phase chemistry from which compounds may be deposited as thin films. The properties of these films are dependent upon the energy of the ablated species.
In this paper we report studies of the plume dynamics of species ablated from titanium targets under KrF (248 nm) laser irradiation at fluences in the 1 to 15 J cm⁻² range.
Ion probes were used to measure the ionised fraction as well as the spatial and velocity distribution of the ablated species. These results are compared with spatial and temporal resolved emission spectroscopy of the luminous species in the plume.
- G-III/P8** A TWO STEPS REACTIVE PULSED DEPOSITION OF HYDROXYAPATITE COATINGS ON METAL SUBSTRATES, V. Nelea, A. Cornet, ENSAIS, 24 Bd. de la Victoire, 67084 Strasbourg Cedex, France; C. Ghica, J. Werckmann, IPCMS-CNRS, 23 Rue du Loess, 67000 Strasbourg, France; C. Martin, I.N. Mihailescu, INFLPR, PO Box MG-36, 76900 Bucharest, Romania
Hydroxyapatite (HA), Ca₅(PO₄)₃OH, has attracted over the past decade much attention as the best substitute material for the human bone tissue. We report a new solution for obtaining stoichiometric and crystalline HA thin layers on Ti. We first create on the metal collector a TiN diffusion barrier by RPLD at room temperature from a Ti target in 4-6 Pa of N₂. We continued with the deposition of HA by RPLD in O₂ at 4-6 Pa. The as deposited Ti support is then heated in air at 500 °C for 30 minutes. We demonstrate by SAED, GIXRD, EDS and TEM that the HA films remained very pure and crystalline. The obtained structures are very adherent to substrates, stable in time and hard.
- G-III/P9** REACTIVE PULSED LASER ABLATION AND DEPOSITION OF THIN ITO FILMS FOR SOLID STATE COMPACT SENSORS, T.M. Di Palma, A. Giardini Guidoni, Dipartimento di Chimica, Università "La Sapienza", Ple A. More 5, 00185 Roma, Italy; V. Marotta, Istituto Materiali Speciali CNR, via S. Loja, Tito Scalo (Pz), Italy; R. Teghil, Dipartimento di Chimica, Università di Basilicata, via N. Sauro 85, 85100 Potenza, Italy
Indium oxide and indium-tin oxide (ITO) have been widely investigated for their use as ceramic sensors, due to their unique optical and transport properties. In this paper studies on deposition of In₂O₃ and ITO films by Reactive Pulsed Laser Ablation (RPLAD) are reported. Thin ITO and In₂O₃ films have been deposited on Si 100 substrates by laser ablating pure metals in oxygen atmosphere. The ablation has been carried out by a frequency doubled Nd-YAG laser and the O₂ pressure has been varied from 50 to 1000 Pa. The substrate temperature has been varied from 25 to 600°C. The deposited films have been analysed by x ray diffraction, scanning electron microscopy and electric resistance measurements.
- G-III/P10** PULSED LASER ABLATION AND DEPOSITION OF BIOACTIVE GLASS AS COATING MATERIAL FOR BIOMEDICAL APPLICATIONS, L. D'Alessio, R. Teghil, M. Zaccagnino, I. Zaccardo, Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, 85100 Potenza, Italy; D. Ferro, CNR Centro di Termodinamica Chimica alle Alte Temperature, Ple A. More 5, 00185 Roma, Italy; V. Marotta, CNR Istituto Materiali Speciali, via S. Loja, Tito Scala (Pz), Italy
Various kinds of bioactive materials have been developed and successfully applied to artificial bones in the last few years. These include sintered hydroxyapatite, glass ceramics and glasses. In this paper a study of the laser ablation and deposition, on Ti-Al substrates, of a biologically active glass suitable for bone implants is reported. The physico-chemical aspects concerning various steps of the process will be analysed. A particular attention is devoted to the optimisation of the experimental parameters, to the analysis of the gaseous phase by mass spectrometry and emission spectroscopy and to the characterisation of the deposits from a compositional and morphological point of view.
- G-III/P11** ON THE GROWTH OF LiF FILMS BY PULSED LASER DEPOSITION, A. Perea, J. Gonzalo, C.N. Afonso, Instituto de Optica (CSIC), Serrano 121, 28006 Madrid, Spain and S. Martelli, R.M. Monteverdi, ENEA, C.R. Frascati, C.P. 65, 00044 Frascati, Italy
Alkali fluoride films coloured by ionising radiation are very promising as tunable active waveguides in the green-red region. They are among the materials with lower refractive index in nature and therefore high dense and compact films are required to produce waveguides with higher refractive index. Since pulse laser deposition (PLD) is known to produce very dense films, it might be a better option than thermal evaporation.
In this work, we will present preliminary results on the growth by PLD of LiF films on native oxide covered Si (100) substrates. LiF is an insulator with an absorption bandgap in the far UV, well beyond the photon energy of excimer lasers. Therefore, the ablation process is expected to occur by different mechanisms than in the common case in which the photon energy is greater than the gap. The influence of several parameters such as the laser energy density, the presence of a gas pressure or the temperature of the substrate, on the film quality is studied, the latter being analysed mainly by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). The films deposited in vacuum are polycrystalline with a pronounced (100) preferential orientation, whereas those grown in He pressure present a more complicated orientation system. Generally the films are optically rough, the roughness decreasing as the substrate temperature increases or the laser energy density decreases. The roughness is related to the special ablation mechanism taking place in the target and possible ways to change it and therefore to improve the smoothness of the films will be discussed.

- G-III/P12** **CHARACTERISATION OF MODIFICATIONS OBSERVED ON NITRIDES AFTER AN UV LASER EXPOSURE**, G. Nicolas, Escuela Politecnica Superior, Universidad de La Coruna, C/ Mendizabal s/n, 15403 Ferrol, Spain; G. Vacquier, Université de Provence, Laboratoire de Physico-Chimie des Matériaux, 3 Place V. Hugo, 13331 Marseille Cedex 3, France; L. Yaghdjian, M. Autric, IRPHE, Laboratoire LP3, 163 Av. de Luminy, 13009 Marseille, France
High energy UV laser pulses are very useful to transform in the near surface region, materials very hard such nitrides with a high precision. By a suitable laser surface treatment, it can be possible to modify the atoms arrangements of the irradiated area and thus to change an insulator in a surface conducting material.
Such investigations have been carried out using a KrF excimer laser (20ns pulse duration FWHM) on nitrides (AlN and Si₃N₄) and the modifications induced by life laser treatment have been expected for each material using advanced surface techniques (SEM, AES, EDS, XRD...). The influence of irradiation parameters and the presence of plasma formation during the interaction processes are also discussed.
One notable result obtained is, for example, the formation of a metallic thin film on aluminium nitride.
- G-III/P13** **DEPOSITION OF SiC AND AlN THIN FILMS BY LASER ABLATION AND SURFACE ACTIVATION**, J. Meinschien, F. Falk, H. Stafast, Institut für Physikalische Hochtechnologie, Helmholtzweg 4, 07743 Jena, Germany
SiC and AlN thin films were deposited on silicon and fused silica substrates by KrF excimer laser ablation from SiC and AlN targets. They were characterized by FTIR and Raman spectroscopy, XRD, RBS, AFM, SEM and TEM.
Improvements in crystalline SiC thin film deposition by laser ablation combined with laser surface activation were reported recently *). These investigations were extended by using an intermediate layer of AlN.
Crystalline AlN films were deposited at substrate temperatures between 700 and 850°C. Modelling of IR reflection spectra revealed that the films are comparable to AlN films prepared by molecular beam epitaxy. Laser activation of the film surface during deposition deteriorates the AlN film properties.
Bilayers of AlN and SiC were deposited on Si substrates at temperatures up to 800°C. At relatively low temperatures an AlN buffer layer improves the quality of SiC films. Laser surface activation was used for SiC film deposition only.
For both materials high deposition rates of 0.3 Å/pulse or 50 nm/min at moderate substrate temperatures were obtained. Thus film preparation for optical applications, where film thicknesses of approx. 1 µm are required, seems to be realistic.
*) M. Diegel, F. Falk, R. Hergt, H. Hobert, H. Stafast, Appl. Phys. A66, 183 (1998)
- G-III/P14** **LASER DEPOSITION OF YBaCuO THIN FILMS -STRESS MEASUREMENTS AND MICROSTRUCTURE INVESTIGATIONS**, R.J. Gaboriaud and F. Pailloux, Université de Poitiers, Laboratoire de Métallurgie Physique UMR 6630, CNRS, SP2MI, Bd 3, téléport 2, BP 179, 86960 Futuroscope cedex, France
Superconducting thin films of YBaCuO has been deposited by laser ablation at 750°C on MgO (001) single crystal. X-ray pole figure indicates a high crystalline quality of C-axis oriented films.
A 4-circle X-ray goniometer has been used for the measurements of the internal stress in the films by mean of the fundamental metric tensor method generally used in the field of continuum mechanic.
Microstructural investigation has been done by HRTEM on plan-view samples in order to study the film-substrate epitaxy relationship from the observation of the moiré pattern brought about by the superimposition of both YBaCuO and MgO lattice (9% misfit).
The results are discussed in terms of crystallographic accommodation and stress relaxation between the film and the substrate.
- G-III/P15** **AN XPS AND XRD STUDY OF PHYSICAL AND CHEMICAL HOMOGENEITY OF Pb(Zr, Ti)O₃ THIN FILMS OBTAINED BY PULSED LASER DEPOSITION**, P. Verardi, F. Craciun, M. Dinescu*, L. Mirenghe**, V. Sandu*, CNR Istituto di Acustica "O.M. Corbino", Area di Ricerca Roma-Tor Vergata, Rome, Italy, *Institute of Atomic Physics, Bucharest, Romania, **PASTIS-CNRS, Brindisi, Italy
Pb(Zr, Ti)O₃ (PZT) oriented films deposited by laser ablation on Au(111)/Si(111) have been tested by different techniques for their physico-chemical homogeneity. The samples have been divided in different zones, in order to verify the existence of chemical and structural differences between different regions. Few techniques, like XRD and XPS have been employed for characterization. XRD analysis shown differences between the crystallographic content and the degree of orientation of zones subjected to plasma flux regions arriving at different angles of incidence on sample surface. In the same zones XPS studies have been performed by a VG ESCALAB 210 Spectrometer, using a non-monochromatic Al Kα X-ray source (300 W) and a five channel hemispherical analyser. Wide scans in the binding energy scale (0, 1200) eV (at 50 eV analyser pass energy) were collected both onto the as received surface and after sputter cleaning in order to put in evidence all the constituents of the film. Narrow scans of Ti2p, Zr3d, Pb4f, O1s and Cls were also acquired at 20 eV and 0.1 eV/channel pass energy and 100 ms of dwell time in order to give a better insight into the chemical bonds formed and a semiquantitative analysis of the present chemical species. The obtained results are discussed in the light of different existing models.
- G-III/P16** **ELECTROLESS METALLIZATION OF CARBON FILMS**, E. Touchais-Papet, M. Charbonnier, M. Romand, Laboratoire de Sciences et Ingénierie des Surfaces, Université Claude Bernard-Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
A new method for promoting electroless metal deposition onto polymer substrates has been recently developed. This process, based on the grafting of nitrogen atoms (via plasma or UV-laser treatment) on the substrates before chemisorption of a catalyst (Pd), takes advantage of the strong chemical affinity of palladium towards nitrogen.
The present work aims at extending the method to other materials, and particularly to carbon.
For this purpose, thin carbon (a-C) and carbon nitride (CNx) films have been deposited onto polycarbonate and glass substrates by DC magnetron sputtering of a graphite target. In the case of a-C films, argon was used as sputtering gas, and electroless metallization was realised through nitrogen atom grafting on the top surface by a subsequent plasma treatment. In the case of CNx coatings obtained by using N₂ both as sputtering and reactive gas (10⁻³ to 5x10⁻¹ Torr), electroless metallization was possible thanks to N atoms present in the films. Deposition parameters of a-C and CNx films were optimised for the metallization purpose itself through XPS analyses and adhesion mechanical measurements.
- G-III/P17** **ENHANCED MAGNETORESISTANCE BEHAVIOUR IN CeO₂ BUFFERED LaCaMnO ON Si GROWN BY PULSED LASER DEPOSITION**, W. Zhang, X. Wang*, I.W. Boyd, M. Elliott** and W. Herrenden-Harkerand**, Department of Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK; *School of Electrical Engineering and Information, South Bank University, 109 Borough Road, London SE1 6UH, UK; **Department of Physics and Astronomy, University of Wales, Cardiff College, Cardiff CF2 3YB, UK
Recent investigations have revealed that direct deposition of colossal magnetoresistance perovskite metallic oxides on Si substrates can produce large magnetoresistive behaviour. For example, a maximum value of 22% has been obtained in the La-Pb-Mn-O system and 35% and 70% values in La-Ca-Mn-O and La-Nd-Sr-Mn-O systems respectively. However this cannot be described as CMR values were present. The lack of CMR effects may be attributed to the imperfect structure introduced by the large lattice mismatch between the film and the substrate.
We have observed the colossal magnetoresistance behaviour on CeO₂ buffered La_{0.70}Ca_{0.30}MnO_{3.5} on Si(100) substrates grown by pulsed laser deposition. A colossal magnetoresistance ratio of Δρ/ρ₀, with more than 96% at 97 K under a magnetic field of 12 T, has been obtained. The dependence of the electrical and the magnetic properties on the post-annealing has also been investigated. Our results suggest that the width of the phase transition can be associated with the structural distortion of the layers.

- G-III/P18** PREPARATION DEPENDENCE OF THE MAGNETIC BEHAVIOUR IN La-Ca- Mn-O FILMS, W. Zhang and I.W. Boyd, Department of Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK; M. Elliott and W. Herrenden-Harkerand, Department of Physics and Astronomy, University of Wales, Cardiff, Cardiff CF2 3YB, UK

The observation of colossal magnetoresistance (CMR) effects in doped perovskite-type La-Ca-Mn-O films has renewed interest in both fundamental condensed matter physics and possible potential applications in the magnetic recording industry. An interesting finding is that their transport properties and magnetoresistance behaviour are extremely sensitive to the preparation of the films. It is not yet clearly understood why and how the electrical properties and magnetoresistive behaviour are so affected by the preparation conditions.

To provide insight into the effect of the preparation conditions, La-Ca-Mn-O films were grown by pulsed laser deposition (PLD) under a wide range of substrate temperatures with other parameters fixed. An increase in resistivity and a decrease in the peak resistivity temperature is found to occur simultaneously with the increase in T_s . The largest MR value, with a 40% ($\Delta\rho/\rho_0$) change in resistivity, appeared in films deposited at 900°C, whilst the largest MR of 20% ($\Delta\rho/\rho_0$) near room temperature was exhibited in films deposited at 500°C. The stoichiometry of elements in the films was also examined specifically. A calcium and oxygen deficiency in the films, produced inherently by the PLD process, can be used to explain the observed phenomena.

- G-III/P19** DUAL BEAM PULSED LASER DEPOSITION OF CRYOLITE THIN FILMS, L. Lambert, M. Autric, IRPHE-LP3, Marseille, France; W. Marine, GPEC, Marseille, France and F. Grangeon, EPFL-CRPP, Lausanne, Switzerland

Cryolite compound (Na_3AlF_6) presents remarkable optical properties (constant low refractive index and transparency over a wide spectral range). To deposit cryolite thin films with the right stoichiometry a Direct Pulsed Laser Deposition (DPLD) set-up and a Dual Beam Pulsed Laser Deposition (DBPLD) set-up have been used. Thin films were deposited in a high-vacuum chamber by ablation of a single cryolite target (DPLD) or simultaneous ablation of two cryolite targets with an angle of about 120° (DBPLD). A silicon substrate is placed just in front of the targets. In the case of DBPLD the two ablation plumes are crossing at few millimeters from the targets. The collision of the two expanding clouds leads to a redistribution of the trajectories of the high-density fast species (atoms and molecules) in the substrate direction. Heavy particles (droplets) interact weakly and their trajectories are not affected. To stop them a diaphragm is placed between the targets and the substrate. Morphology, structure and composition of thin films have been analysed. First results show that thin films produced by DPLD and DBPLD present a composition close to the bulk stoichiometry. With the DPLD method thin films surfaces present a high density of droplets. At the opposite with the DBPLD technique a dramatic decrease of the droplets density is observed. Moreover series of fast CCD photographs confirm the redistribution of trajectories of ablated species due to the collision of the two plasmas clouds.

- G-III/P20** FUNDAMENTAL MECHANISMS IN LASER-INDUCED ABLATION OF METALS: DEFECT INITIATED BOND BREAKING, E. Stietz, M. Stuke*, J. Viereck, T. Wenzel and F. Träger, Fachbereich Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany; *Max-Planck-Institut für biophysikalische Chemie, P.O. Box 2841, 37018 Göttingen, Germany

- G-III/P21** THE FORMATION OF ALTERED LAYER DURING THE REACTIVE ION ETCHING OF $\text{Al}_{III}\text{B}_V$, A. Grigonis, A. Galdikas, M. Silinskas, Physics Department, Kaunas University of Technology, Studentu 50, 3031 Kaunas, Lithuania

The reactive ion etching of GaAs (100) in $\text{CF}_2\text{Cl}_2 + \text{O}_2$, $\text{CF}_4 + \text{O}_2$ and O_2 plasma is considered. The RF plasma was created in diode asymmetrical system and plasmatrone with ion accelerating potential of 100-1500 V discharge power of 0.5-5.0 W/cm² and at pressure of 10⁻²-10 Pa. experimental measurements have shown that with increasing of discharge power in plasma O_2 up to >0.75 W/cm² the quantity of arsenic oxide decreases and the surface is enriched by polycrystalline gallium oxide. The process of reactive ion etching becomes more intensive due to volatile arsenic compounds with the addition of chlorine and fluorine compounds into the oxygen plasma. The layer containing the mixture of Ga_2O_3 , GaO , Ga_2O_3 with complex crystallographic structure obtains at more intensive ion bombardment. The experimental curves were modeled by proposed phenomenological model including sputtering, implantation, adsorption, heterogeneous chemical reactions, desorption of volatile compounds and radiation enhanced diffusion. The balance equations are written for each component in each monolayer. The model gives the kinetics of elemental composition on the surface and the composition of the altered layer.

- G-III/P22** PHOTOCHEMICAL CROSSLINKING OF POLYDIMETHYLSILOXANES, S. Luzgarev and V. Denisov, Kemerovo State University, Krasnaya street 6, 650043 Kemerovo, Russia

Crosslinking of polydimethylsiloxane rubbers in the presence of aromatic carbonyl compounds (almost twenty 9,10-anthraquinones, anthrones and their derivatives) under the effect of UV light of Hg-lamps of low and medium pressure has been studied using sol-gel analysis, UV and IR spectroscopy.

The results show the influences of properties of polydimethylsiloxanes, nature and structure of initiators on their chemical and photochemical reactions, which differ from analogous reactions in other polymers (for example, polyethylene). Photoreduction with formation of free anthrahydroquinones and anthranols is the main reaction. At the stage of their photoreduction, crosslinking yields increase with the growth of compatibility of initiators in polydimethylsiloxane.

Influences of nature and structure of initiators, their concentrations, temperature of process and presence of oxygen on speed of crosslinking and hardening, properties of siloxane coatings and films were studied.

The researches showed possibility production of thermostable protective and insulating coatings and films which have good adhesion and mechanical strength on various materials with a wide range of physico-mechanical properties - from soft and elastic to rigid and firm ones.

- G-III/P23** PLASMA ANALYSIS IN THE PROCESS OF REACTIVE LASER ABLATION FOR NANOSIZE AlN SYNTHESIS, I. Apostol, C. Grigoriu, D. Dragulinescu, C. Luculescu, S. Udrea, National Institute for Laser, Plasma and Radiation Physics, PO Box Mg 36, 76900 Bucharest, Romania

Nanosize materials synthesis by reactive laser ablation has become a field of growing interest. Our work was confined on AlN powder synthesis by laser ablation of an Al target in nitrogen environment under the action of excimer laser (wavelength 248 nm, pulse duration 20 ns, fluence 2.5 J/cm²). The major interest is in controlling material properties (size distribution, composition, etc.) and in improving the production reliability at lower cost. For this reason the influence of laser target interaction and formation of many-particle systems was studied by analysing the emission properties of the ablation plasma. Optical spectroscopy of plasma represents a fast in-situ diagnostic method which gives information about the laser-target and the laser-plume interactions. In the gas dynamics process are taking place phenomena which are important to the material synthesis and space and time evolution of plasma emission gives information about the evolution of the composition of the plasma plume. In case of AlN powder synthesis we have analysed the dynamics of Al atoms and ions to select the proper incident laser energy range as a function of ambient gas pressure. These results are discussed in correlation with quality of the resulted AlN nanosize powder. Spectroscopic measurements revealed the space and time distribution of neutral and ionise atoms, which were analysed as a function of experimental conditions.

- G-III/P24** **OXIDATION PROCESS IMPROVEMENT IN PULSED LASER DEPOSITION OF THIN FILMS**, I. Apostol, R. Stoian, C. Luculescu, R. Dabu, A. Stratan, S. Udrea, National Institute for Laser, Plasma and Radiation Physics, Laser Dept., PO Box MG 36, 76900, Bucharest, Romania
Deposition of thin films using laser ablation has become a suitable technique especially for multicomponent materials, due to instantaneous material removal and target similar stoichiometric deposition. In case of superconducting YBCO the as-deposited thin films generally present an oxygen deficiency which is altering the superconducting properties. As the oxygen concentration is dictated also by the kinetic of oxidation during plasma expansion time we have used a transversal IR irradiation beam simultaneously with the UV laser beam producing the plasma, focused in front of the plume for oxygen dissociation and atomic oxygen formation as a method for oxidation improvement by gas phase interaction during the material transport from the target to the substrate. Oxides enhancement has been analysed by optical spectroscopy. Spatially resolved measurements have revealed that the composition of the plume expanding in an oxygen environment is changed in favour of oxides for distances from the target surface which exceeds the region of IR laser beam focusing. In the neighbourhood of the target surface the composition of the plume as results from the analyses of the optical emission remains unchanged. It is supposed that in the IR irradiation regime the oxygen molecule will dissociate under the effect of laser beam, leading to atomic oxygen formation with an enhanced oxidation efficiency.
- G-III/P25** **ULTRASONIC INVESTIGATION OF PULSED LASER INTERACTION WITH SOLID TARGETS**, I. Apostol, R. Stoian, S. Ersen, R. Dabu, A. Stratan, National Institute for Laser, Plasma and Radiation Physics, Laser Dept, PO Box MG 36, 76900, Bucharest, Romania; A. Serbanescu Oasa, Technical University, Sibiu
During the complex process of laser interaction with solid targets elastic waves are induced in the volume materials and their waveforms and intensity were used to characterise the phenomena taking part in the interaction region and the quality of the irradiated material surface. During the pulsed high power laser target interaction due to the small laser spots and short duration of laser pulse a local surface heating or material ablation takes place depending on the incident laser energy density. In both cases a stress wave is induced in the material volume with characteristics determined by the phenomena taking place in the interaction region. Analyses of the detected acoustic wave first peak amplitude and especially of the region of the transversal wave appearance resulted in a method of interaction regime characterisation, ablation threshold determination and multipuls processes in-situ monitoring. We have determined the ablation threshold for metallic samples correlated with the target surface quality and laser radiation coupling with materials was analysed. In case of small incident laser energies a preblative region is evidenced and the importance of this phenomena for the multipulse process is discussed.
- G-III/P26** **ELECTROCHEMICAL DISSOLUTION AND DEPOSITION OF DOPED p- AND n-SILICON IN ANHYDROUS ORGANIC SOLUTIONS**, J. Banas and U. Lelek-Borkowska, University of Mining and Metallurgy, Faculty of Foundry Eng., Dep. of General and Anal. Chem., ul. Reymonta 23, 30-059 Cracow, Poland
In this paper the anodic etching of p- and n- doped silicon in anhydrous organic solutions with absence of fluorides and the possibility of electrodeposition of silicon on platinum in these media are discussed. Experiments were performed on p- and n-Si wafers (110) oriented in anhydrous deaerated solutions of LiCl, HCl, LiClO₄ and H₂SO₄ in methanol, acetonitrile, formamide and n-dimethylformamide. These organic media were chosen with regard to their dielectric permeability and character (protogenic or not). The linear sweep voltammetry LSV and potential transient techniques were used in research. Etched silicon surface was examined by means of the X-ray photoelectron spectroscopy (XPS). The presence of silicon layer on platinum surface was confirmed by LSV and X-ray analysis. The anodic dissolution of p-Si in anhydrous organic solutions of chlorides proceeds via consecutive reactions: Si→Si(II)→Si(IV) with participation of chloride ions. The XPS measurements show that silicon surface etched at potential 1,0 V is covered with thin anodic film consisting mainly of Si(II). At „transpassive” potential (2,5 V) the anodic film consisted of Si(IV) is thicker and doesn't contain Si(II) species. The mechanism of anodic dissolution is proposed. Investigations presented in this paper proves that as well the anodic etching of silicon surface as deposition of silicon in anhydrous organic solutions of chlorides is possible.
- G-III/P27** **VACUUM ULTRAVIOLET ANNEALING OF THIN FILMS GROWN BY PULSED LASER DEPOSITION**, V. Craciun and D. Craciun, Laser Dept, NILPRP, Bucharest V, Romania; P. Andreazza, CRMD, University of Orleans, Orleans, France; J. Perriere, GPS, Universite Paris VII, Paris, France; I.W. Boyd, Department of Electronic and Electrical Engineering, UCL, Torrington Place, London WC1E 7JE, UK
Pulsed Laser Deposition (PLD) is one of the most suitable techniques for the growth of high quality thin films. To obtain stoichiometric, good crystalline films, a reactive atmosphere simultaneously with relatively high substrate temperatures are sometimes required during the process. These conditions could be too harsh for some substrate materials, like in the case of hydroxyapatite growth on Ti which is oxidised, resulting in poor adhesion and bio-compatibility problems. In addition, the growth rate decreases with the increase of substrate temperatures which will set a practical limit to the thickness of the grown films.
The effect of a post-deposition vacuum ultraviolet (VUV) annealing treatment in 1 bar of oxygen at modest temperatures (>475 deg C) on the properties of ZrO₂ and hydroxyapatite films grown by PLD (KrF laser, 1-5 J/cm²) was investigated. The VUV radiation dissociates the oxygen molecules and forms ozone and atomic oxygen which are more reactive than O₂, helping the oxidation reaction to proceed faster at low temperatures. The optical properties of the grown Zr O₂ films improved significantly after the VUV anneal, while in the case of hydroxyapatite films a change of the crystalline structure was evidenced.
- G-III/P28** **GROWTH OF THIN TRANSPARENT TITANIUM NITRIDE LAYERS BY REACTIVE LASER ABLATION**, V. Craciun, D. Craciun, Laser Dept, NILPRP, Bucharest, Romania; C. Ghica, L. Trupina, NIMP, Bucharest, Romania; C. Fluieraru, N. Nastase, IMT, Bucharest, Romania
Transparent conductors are used for solar cells, wiring in display panels, heaters and other applications. The commonly used materials for these applications, indium tin oxide (ITO) has a poor corrosion resistance whilst thin gold films have a low mechanical resistance. TiN is particularly suitable for transparent conductive films as it is a hard material, exhibiting excellent corrosion and wear resistance. As layer by layer growth can be promoted by high supersaturation ratios and high energy atoms or ions, the pulsed laser deposition (PLD) method was used for obtaining very thin, transparent and conductive TiN films. To reduce the droplet density on the surface of the grown films, a reactive PLD, where a massive, high density Ti target was ablated in a N₂ atmosphere, was employed. Scanning and transmission electron microscopy, electron diffraction, optical transmittance, four point probe and atomic force microscopy techniques were used to characterise the properties of the grown films.
- G-III/P29** **RF PLASMA TREATMENTS OF MACROMOLECULAR MEMBRANES**, E. Aldea, G. Dinescu, B. Mitu, National Institute of Lasers Plasma and Radiation Physics, Atomistilor 1, MG 36, 76900 Magurele, Bucharest, Romania; G. Popescu, A. Bujor, D. Rată, Research Center for Membranes and Macromolecular Materials, Bucharest; M. Olteanu, Dept. of Chemistry, University of Bucharest, Romania
RF plasma treatments of the active surface of polysulfone membranes in air and air-monomer mixtures have been performed. The experimental conditions were: RF power 10-50 Watt, pressure 0.1-1 mbar, monomer flow 0.05-2 sccm.
Plasma was investigated using optical emission spectroscopy. Using computer-simulated spectra of N₂⁺ and CN violet systems rotational and vibrational temperatures were determined. The effects of treatments, on the membranes properties, have been investigated by permeation of gases and liquids. Pore radius, pore density and active layer thickness were calculated from these measurements. Mass gravimetry, infrared absorption spectroscopy, scanning electron microscopy (SEM) and contact angle measurements have been used to obtain information about the surface modifications.
The structural changes of membranes top layer are associated with a competitive process between plasma ablation of the membrane material, redeposition of the ablated material as a thin layer on the membrane surface and polymerization of the external monomer.

- G-III/P30** SOME PARTICULAR ASPECTS OF POLYSILICON GATE PLASMA ETCHING PROCESS IN CMOS TECHNOLOGIES, I. Cernica, C. Dunare, Liviu Bocioaca, National Institute of Microtechnology, PO box. 38-160, Bucharest, Romania
The plasma etches of gate polysilicon represents one of the most sensible process in CMOS technology. We investigate the aspects regarding the correlation's between the process parameters and the final failing rate of the CMOS integrated circuits. The aims of this paper is to propose an optimized process for etching polysilicon gate and to underline a possible cause for gate-source/drain scc apparition. It has been presented different plasma etch processes varying etch parameters. It was measured the etching nonuniformity, substrate damage and underetching, phenomena which altered the electrical device yield. The measurements was done both electrical (functional and parametric tests on wafers) and by microscopy (including SEM investigations). The obtained results allowed to establish an optimized process for polysilicon gate plasma etch which gave the lowest values for underetching and lower dimensional dispersion on wafer. During the experiments we had observed an undergate parasitic etch, phenomenon which could be responsible of gate/source/drain scc.
- G-III/P31** ANALYSIS OF THICKNESS PROFILES OF PULSED LASER DEPOSITED METAL FILMS, Z. Kantor, T. Szörényi*, Z. Toth* and L. Gombos, Department of Optics and Quantum Electronics, Jozsef Attila University, *Research Group on Laser Physics of the Hungarian Academy of Sciences, POB 406, Szeged, 6701, Hungary
When using a liquid (molten) target instead of a solid material, the problem of target deterioration in PLD is completely solved. Ablation from a really smooth surface is the straightforward case that realizes the initial conditions of practically all theoretical considerations. Therefore, liquid-target PLD allows for fair comparison of experiment and theory, e.g. fitting the thickness profiles with mathematical functions that bear real physical meaning. Indium films are deposited by pulsed laser deposition (PLD) in vacuum using a molten In target. The film thickness profiles are derived from two-dimensional optical density maps and profilometric data and are analysed in terms of cosine power functions most frequently used in the PLD literature and Lorentzian-like functions, derived from the so-called elliptical velocity distributions.
- G-III/P32** LASER SOLID-PHASE DOPING OF SEMICONDUCTORS FOR MICROELECTRONIC DEVICES FABRICATION, A.Yu. Bonchik, S.G. Kiyak, A.V. Pokhmurska, G.V. Savitskij, Institute for Applied Problems of Mechanics and Mathematics, 3 b Naukova Street, 290601, Lviv, Ukraine
The present day tendencies in development of semiconductor electronics and microelectronics are concerned above all with transition to the region of submicron dimensions. The transition requires the utilization the technology of new and nontraditional methods of material processing. Using 1 kW CO₂ laser we have fabricated ultra-shallow p-n junctions in Si, GaAs, GaP and InP. SIMS and Auger electron spectrometer were used to measure the depth profiles of the incorporated impurities: boron into Si, Zn into GaAs, GaP and InP. UV photo-diode devices were prepared using this structures. CO₂ laser has been successfully used for irradiation of Ni-Ge: Au-Au structures on InP and hight quality Ohmic contacts have been obtained. A study of the electric properties of diode structures was performed on mesa-diodes obtained by the method of chemical etching, and planar diodes formed by means of laser stimulated diffusion of dopants into semiconductors through windows opened in a protecting coating of SiO₂ or Si₃N₄. Investigations by the AES method have shown that during solid phase diffusion locally doped regions almost exactly reproduce the shape and size of the windows in the dielectric.
- G-III/P33** SOI SPECIAL SENSITIVITY PHOTODETECTORS, I. Lytvyn, Scientific Research Centre TernoCENTR, 11 Lvivska st., TANE, 282004 Ternopil, Ukraine
Developed mathematical model and experimental investigation indicate that photodetectors produced by the laser or lamp recrystallization of thin films poly-Si on insulator have the special controlled sensitivity by a new physical principles of photodetectors operations. Such photodetectors can provide the functions, to transform into the current the information about the light intensity through its distribution on the surface coordinates of sensor and on it spectral content. In sensors application an important advantage is the possibility of an original solution of the transformation procedure of the signals from photodetector with the special sensitivity. According to experimental results the developed photodetectors with special sensitivity can give a possibility to alleviate the problem to reduce the understanding time of the vision systems in comparison with conventional navigator design. Paper describes also peculiarity of fabrication methods of photodetectors with special sensitivity.
- G-III/P34** EPITAXIAL GROWTH OF DIELECTRIC SrTiO₃ THIN FILMS BY PULSED LASER DEPOSITION, Tao Yu, Yan-Feng Chen, Zhi-Guo Liu and Nai-Ben Ming, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R.China
SrTiO₃ is a typical dielectric material in perovskite structure. It can be used as dielectric layer in many device applications. The study of growth of high quality dielectric SrTiO₃ thin films is an important topic. In this article, the epitaxial growth of SrTiO₃ thin films on (001)LaAlO₃ substrates on the basis of optimization of pulsed laser deposition (PLD) processings will be reported. Several analytical techniques, such as X-ray diffraction Θ -2 Θ scan and Φ scan, AFM, XPS was used for analyzing the epitaxial property, growth mechanism and surface composition of SrTiO₃ thin films
- G-III/P35** ACOUSTIC PROPERTY OF PbTiO₃/SrTiO₃ MULTILAYER STRUCTURES PREPARED BY MOCVD AND PLD METHODS, Tao Yu, Yan-Feng Chen, Zhi-Guo Liu and Nai-Ben Ming, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R.China
PbTiO₃/SrTiO₃ (PT/ST) multilayer structures was fabricated on Pt/SrTiO₃ and Pt/LaAlO₃ substrates, the PT layer was prepared by MOCVD and the ST layer was prepared by pulsed laser deposition. The typical thickness of PT and ST was 1000Å, the periodic number was 3, 5, 8, 10, respectively. XRD Θ -2 Θ scan results indicated that the PT layers in these multilayer structures were (001) oriented. Using the PT/ST multilayer structures, a set of resonators have been made. The high-frequency resonance properties were analyzed with a HP 8510C network analyzer.
- G-III/P36** OXIDE LAYER GROWTH DYNAMICS INDUCED BY LASERS, L. Fabian*, K. Feher*, Cs. Beleznai*, R. Vajtai*, D. Vouagner** *Department of Experimental Physics, Jozsef Attila University, 6720 Szeged, Dom t. 9., Hungary; **Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard-Lyon 1, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
Instability effects resulted in laser oxide formation on metallic (V, Co, W, etc.) surfaces observed both in solid and liquid phases are presented. The oxidation process induced by laser radiation (CW and/or pulsed) in air, occurs according the Wagner rule, showing all characteristics of positive feedbacks arisen between the optical and thermal channels of the interaction. As a result we could demonstrate the existence of a control parameter leading to the appearance of different events; regular, quasiregular and chaotic oscillations of the temperature function of the sample. At temperatures higher than the melting point of oxide formed due to its high viscosity value we could observe different hydrodynamic type of instabilities such as Marangoni and Taylor vortices as well as hot filament formation in liquid phase. We also demonstrate that the appearance of observed events are due to nonlinearities and nonequilibria of the system leading to thermodynamic conditions far from equilibrium as a result of local heat absorption by laser irradiation.

- G-III/P37** UV LASER-INDUCED ETCHING AND METAL SEEDING ON POLYMERS; A SURFACE CHARACTERIZATION, J. Békési, K. Kordas, Cs. Beleznai, K. Bali and L. Nanai, Department of Experimental Physics, Jozsef Attila University, 6720 Szeged, Dom t. 9., Hungary
Results of UV (308 nm) laser pulse induced dry etching with subsequent Pd deposition from a PdCl₂ solution (acid base with a pH=1) on polyimide surface are reported. The surface roughness has been determined before and after illumination with a fractal-based examination technique using the area-perimeter and the structure function methods. It could be concluded that the preetching of the polyimide surface significantly enhances the flux of Pd atoms deposited onto the surface, which is a power function of the number of shots (30 mJ/cm² at 20 ns pulse duration) with a power coefficient close to 0.5. It has been observed that the seeding process started simultaneously at number of places resulting in island-like deposits. Fractal characterization of surfaces resulted in a fractal dimension close to 2.57 and 2.59 carried out with the methods outlined earlier. It might be concluded that the seeding process occurs at atomic scale, but it exhibits a very strong trend towards the formation of aggregates and/or cluster-type structures.
- G-III/P38** PULSED LASER DEPOSITION OF LITHIUM NIOBATE. A PARAMETRIC STUDY, D. Ghica, A. Cavaleru, INOE, PO Box MG-22, 76900 Bucharest, Romania; C. Ghica, IPCMS-CNRS, 23 Rue du Loess, 67037 Strasbourg Cedex, France; V. Nelea, ENSAIS, 24 Bld. de la Victoire, 67084 Strasbourg Cedex, France; C. Martin, I.N. Mihailescu, INFLPR, PO Box MG-36, 76900 Bucharest, Romania
LiNbO₃ thin films were obtained on Si substrates by pulsed laser deposition. An KrF laser was used at a fluence of 4 J/cm². Stoichiometry and crystallinity of the films were studied as a function of substrate temperature, oxygen pressure, target-collector distance, post-annealing conditions. Different techniques were used to analyse the LiNbO₃ films: grazing incidence X-ray diffraction (GIXRD), X-ray fluorescence (XRF), cross-section transmission electron microscopy (XTEM) and energy dispersive X-ray spectroscopy (EDS).
- G-III/P39** GENERATION OF DONOR CENTERS AT THE SURFACE OF p-InSb BY LASER RADIATION, A. Medvid', L. Fedorenko, Riga Technical University, la Kalku Str., Riga 1658, Latvia
Laser donor centers (LDC) in p-InSb are formed by strongly absorbed radiation of rubin[1], neodimium [2] lasers, and also by weakly absorbed radiation of CO₂ laser [3]. The nature of these centers is still unclear.
The aim of our investigation is to determine parameters of LDC. Experiments are carried out on p-InSb samples in temperature range 180-290K. The current-Voltage characteristics (CVC) and Gauss-Ampere characteristics (GAC) are made in magnetic field below 1 T and in electric field below 100 V/cm. Two types of LDC are observed by YAG:Nd laser radiation ($\lambda=0.53 \mu\text{m}$, $t=15 \text{ ns}$): stable LDC up to temperature 670 K, and unstable LDC annealed at 300 K. The threshold of formation of LDC is 1.5 MW/cm². Investigation of CVC and GAC showed that the depth of localization of p-n junction depends on intensity of laser radiation. Activation energy of stable LDC is approximately 1.1 eV. Recombination time of unstable LDC is 5 s. It is expected that the mechanism of formation of LDC is the drift of Sb vacancies (V_{Sb}) in inhomogeneous temperature field in the volume of the semiconductor. The kinetics of distribution of V_{Sb} in temperature gradient was carried out theoretically at $\Delta T=400\text{K}$ and $\Delta T=500\text{K}$.
1. L.L.Fedorenko, V.K.Malyutenko. Ukrainian Phys. J., 20, 2040 (1975).
2. V.A.Bogatyryov, G.A.Kachurin. Phys. Techn.Semicond, 11, 100 (1977).
3. A.G.Vasiliev et al., Laser Processing and Diagnostics, Berlin, 67 (1984).
- G-III/P40** EXCIMER LASER STRUCTURING OF NEW COMPOSITES MATERIALS, G.V. Danev, E.M. Spassova, J.J. Assa, I.D. Zenov, Bulgarian Academy of Science, 1113 Sofia, Bulgaria and J. Ihlemann, Laser- Laboratorium-Goettingen e.V., 37077 Goettingen, Germany
New bulk polyimide systems prepared by pressing of monomers mixtures have been investigated. A polyimide matrix displaying an amorphous structure is formed as a result of a reaction in a solid phase.
The possibility for excimer laser fabrication by drilling at various diameters and depths is demonstrated. The SEM observation reveals alterations in the thus formed blind hole bottom and surface structures as a consequence of the laser action parameter variations. The changes observed and the dependencies obtained are discussed as a possible result from the number and energy of the laser impulses. Biocompatibility investigations on the studied samples are under way as well as probing for the possibilities for creation of composite Polyimide-Al; Polyimide-C bulk materials.
- G-III/P41** DISCHARGE CHARACTERISTICS OF THE DOUBLE CLOSED-DRIFT ION SOURCE, D.A. Kotov, I.V. Svadkovski, A.P. Dostanko, Belarussian State University of Informatics and Radioelectronics, P. Brovka Street 6, 220027 Minsk, Belarus
High-current, low energy ion source for ion beam assisted deposition using inert and active gases, was developed and investigated. Basic distinction of the developed sources is the extended range of ion energies in high-current beam for optimization of deposition, cleaning and etching processes.
Three-pole-face magnetic system allows to vary the magnetic field direction in the discharge region for control the ion energies within wide limits (25-1100eV) at ion beam current up to 1A. Has been found that the average energy ions at various modes operation was 0.3-0.7 of the anode potential. Having two anodes and the annular acceleration channel provide the operative control of the ion beam profile.
- G-III/P42** PARTIAL AMORPHISATION OF CoSi₂ THIN LAYER BY LASER QUENCHING, M. Knite, M. Ogrinsh, Riga Technical University, la Kalku str., Riga 1658, Latvia and V. Snitka, Kaunas University of Technology, 65, Studentu str., 3031 Kaunas, Lithuania
It is known that crystalline CoSi₂ can be formed from Co + 2Si mixture by laser radiation. The reverse process, i.e. amorphisation or generation of defects is of great importance in microelectronics and optoelectronics as one restoring the electrical parameters.
Thermally grown CoSi₂ layers on SiO₂/Si substrates of thickness 100 nm have been irradiated with Q-switched Nd:YAG laser pulses of 15 ns duration and power ranging from 12 to 40 MW/cm².
The laser irradiated samples were analyzed using atom force microscopy (AFM), X-ray diffraction, infrared reflection spectroscopy, and surface electrical resistivity measurements.
The AFM micrographs reveal two types of surface morphology: pyramid-like cells (diameter 100 nm, height 20 nm) and rampart-like cells (width 600 nm, height 50 nm). The X-ray diffractograms and infrared reflection spectra confirm increasing concentration of defects as well as mechanical stresses in CoSi₂ crystalline layer resulting in the increasing electrical resistivity of CoSi₂ layer.

POSTDEADLINE POSTERS:

- G-III/P43** RAPID PROTOTYPE FABRICATION OF SMOOTH MICROREACTOR CHANNEL SYSTEMS IN PMMA BY PULSED VUV LASER ABLATION AT 157 NM FOR APPLICATIONS IN GENOME ANALYSIS AND BIOTECHNOLOGY, M. Lapczyna, T.Wenzel, M. Stuke, Max-Plank-Institut fuer biophysikalische Chemie, AG Laser Chemical Processing, P.O.Box 2841, 37018 Goettingen, Germany

Submicrometer resolution microreactor channel patterns in PMMA (Polymethylmetacrylate) substrates are generated using a combination of vacuum-ultraviolet (VUV) pulsed laser ablation and laser direct write patterning of a silicon membrane contact mask. First, silicon membranes (thickness 5 ... 12 μm) are exposed in chlorine gas to focused laser light at 514 nm and thereby cut by laser direct write. Virtually any pattern can be generated since the silicon membranes are mounted on precisely controllable xyz-stage. In the second step, the processed membranes serve as contact masks on PMMA substrates for VUV laser ablation at 157 nm (F2 excimer laser). In contrast to conventional etching techniques, the ablation depth within one pattern can be varied on demand. The ablated surfaces feature excellent smoothness (roughness of only a few nanometers). Biocompatible and smooth microchannel systems in PMMA with excellent optical properties - suitable for single molecule detection experiments - have been generated. Including pattern design, fabrication and testing of these structures take less than one day.

- G-III/P44** SHORT PULSE UV LASER ABLATION OF LIQUID AND SOLID GALLIUM, I.Zergioti, M.Stuke, Max-Plank-Institut fuer biophysikalische Chemie, P.O.Box 2841, 37018 Goettingen, Allemagne

A comparative study of the UV laser ablation of solid and liquid Gallium is reported. The ablation was performed by 248 nm excimer lasers with pulse durations of 15 ns and 500 fs. The ablated neutrals were ionised by resonant multiphoton ionisation using a time delayed laser and were detected by time-of-flight mass spectroscopy. This work is complementary to the short pulse UV laser ablation of solid and liquid of Indium which has been already reported [1]. The ablation threshold fluences were measured at 12 mJ/cm² for liquid and at 17 mJ/cm² for solid Ga for the ns laser ablation experiments. The ablation threshold fluence in the fs laser case was measured for both solid and liquid phases at 2.5 mJ/cm². The difference in the energy fluence threshold for fs and ns laser ablation is due to the higher thermal diffusivity and energy dissipation during longer laser pulses. The time of flight measurements show thermal behaviour of the ablated Ga atoms in both fs and ns laser ablation and were fitted as Maxwell-Boltzmann distributions. A linear dependence of the temperature as a function of the ablation laser fluence is observed.

[1] T.Goetz, M.Stuke, Applied Physics, A64 (1997), 539-543.

E-MRS'98 SPRING MEETING



SYMPOSIUM H

Materials Aspects in Microsystem Technologies

Symposium Organizers

- D. BARBIER** Laboratoire de Physique de la Matière, INSA, Villeurbanne, France
- W. LANG** HSG-IMIT, Villingen-Schwenningen, Germany
- J.R. MORANTE** Universitat de Barcelona, Barcelona, Spain
- D. ESTEVE** LAAS, Toulouse, France
- G. MUELLER** Daimler-Benz AG, München, Germany

SYMPOSIUM H

Tuesday June 16, 1998
Mardi 16 juin 1998

Morning
Matin

SESSION I - Devices I

- H-I.1** 8:30-9:10 -Invited- **SILICON COMPATIBLE MATERIALS FOR HARSH-ENVIRONMENT SENSORS, G.H. Kroetz and M.H. Eickhoff, Daimler-Benz AG Research and Technology, Dep. FT2/M, Postbox 80 04 65, 81663 Munich, Germany**
The application of pure silicon sensors is limited to temperatures below 150°C. This matter of fact substantially reduces the field of applications and the accessible market. Especially in automotive applications temperatures between 150°C and 800°C are nothing unusual. Materials are required, which extend the applicability of micromachined silicon sensors to higher temperatures and which are compatible to silicon and silicon processing steps. They have to fit to standard micromachining processes and apart from the deposition equipment no special processing tools should be necessary, in order to keep investment costs low. There is a choice of several materials fulfilling these conditions to varying degrees. The present talk will give an overview of these and weigh up the advantages and disadvantages. The presentation is concerned specifically with silicon on insulator, silicon carbide on silicon and insulator, GaN and diamond on silicon. In detail the mechanical, thermal and sensory properties of these materials will be treated in a comparative manner and examples of applications in automotive systems will be given. Furthermore the commercial availability of the different materials in form of substrates will be regarded and a forecast of future developments will be tried.
- H-I.2** 9:10-9:30 **IMPROVED SIMULATION FOR STRONGLY COUPLED MEMS: RESONANT VACUUM SENSOR OPTIMIZATION, B. Folkmer, A. Siber*, W. Große-Bley**, W. Lang, HSG-IMIT: Hahn-Schickard-Gesellschaft, Institut für Mikro- und Informationstechnik, W. Schickard-Str. 10, 78052 Villingen-Schwenningen, Germany; *Gesellschaft für Sensoren mbH, Villingen-Schwenningen, Germany; **Leybold Vakuum GmbH, Köln, Germany**
The paper describes a new approach for simulation and optimization of micro-electro-mechanical systems (MEMS) with strongly coupled physical behaviour. By the use of commercial analysis tools only, without any specific add-ons, MEMS simulation can be carried out to the end of system simulation. The combination of general purpose finite-elements analysis with multi-physics system simulation is successfully demonstrated. The new method is applied for the analysis of a resonant total pressure sensor systems. The sensor is a resonator fabricated in bulk silicon technology. The total pressure influences the resonance frequency and height due to thermal interaction and friction. The pressure characteristics of the complete system was measured in good agreement with the system simulation results.
- H-I.3** 9:30-9:50 **OPTIMIZING PHOTODIODE ARRAYS FOR THE USE AS RETINAL IMPLANTS, M.B. Schubert, A. Hierzenberger, H.J. Lehner, J.H. Werner, Universität Stuttgart, Institut für Physikalische Elektronik, Pfaffenwaldring 47, 70569 Stuttgart, Germany**
The basic function of photoreceptors in the human eye is very similar to that of solar cells, namely delivering potential changes upon illumination. The quantum efficiency of photoreceptor action, however, is 1000 times larger than that of the corresponding technical devices. Therefore the intriguingly simple approach of replacing degenerated photoreceptors by artificial solar cell arrays has to overcome some difficulties, especially the energy supply for retina stimulation. Recently we have developed ultrathin and flexible microphotodiode arrays on the basis of amorphous silicon (a-Si) pin structures, with openings for retina tissue nourishment. We now report on the functional optimization of several aspects of these devices. First, the long-term stability in the physiological environment has to be assured. Since plasma deposited silicon nitride (SiN) is not stable over periods of several months, we now use high-density sputtered SiN as a protecting layer. The main emphasis of this study is put on the additional energy supply of the implants by means of near infrared radiation. First experiments address the problem of local light-induced switching of an a-Si photoconductor on top of an IR-sensitive crystalline silicon pin cell. Proper operation can only be achieved if band discontinuities are minimized, therefore buffer layers, a-SiGe photoconductors, and nip infrared diodes are investigated. This contribution is based on our joint research with several institutions, coordinated by E. Zrenner at the University Eye Hospital Tuebingen, and funded by the German BMBF.

H-II.4 9:50-10:10

MICROSTRUCTURES OF THE MONOMORPH PIEZO-ELECTRIC CERAMIC ACTUATORS WITH FUNCTIONAL GRADIENTS, Xinhua Zhu, Jianming Zhu, Shunhua Zhu, Qi Li and Zhiguo Liu, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

Recently micro-electromechanical systems (MEMS) have been attracted in various fields. The importance of the microactuators utilizing piezoelectricity as the driving elements in MEMS have been increasing. Piezoelectric actuators are usually constructed as either stacked or bimorph forms. For those actuators, they usually have an uneven distribution of stresses when voltage is applied, which could lead to lifetime limitations of devices. It is very desirable to develop a monomorph with few or no internal stress peaks when voltage is applied and no structural joint that can result in failures of devices with repeated strain reversals. In this paper, a monolithic ceramic bar with a gradient of piezoelectric activity across its thickness is introduced, which is fabricated by the interdiffusion between a high piezoelectric and dielectric compositions. The monomorph is to bend due to the differential stresses induced by the applied voltage. The microstructures of the interdiffusion layer have great effects on the electric field-induced displacement characteristics and interfacial strength of the monomorph piezoelectric actuator. The compositional profiles, phase distributions and short range phenomena in the interdiffusion layer formed in the PZT/PNN ($\text{PbNi}_{1/2}\text{Nb}_{3/2}\text{O}_3$: PNN) monomorph ceramic actuators with functional gradients are investigated by EPMA and TEM respectively. The results show that the thickness of the interdiffusion layer (d) for different diffusing ions can be ordered as $d\text{Ni}^{2+} > d\text{Nb}^{5+} > d\text{Ti}^{4+} > d\text{Zr}^{4+}$. An interface between the rhombohedral and pseudocubic phases is found to exist in the interdiffusion layer by TEM observations and selected area electron diffraction (SAED) patterns. The SAED studies also reveal the presence of the $1/2 [111]$ superlattice spots along the $[111]$ direction of perovskite cubic unit cell, and the origin of the superlattice is determined.

10:10-10:50

BREAK

SESSION II - Devices II

H-II.1 10:50-11:10

MICROMACHINED SWITCHING CONTACTS FOR LOW ELECTRIC LOADS, K. Hiltmann, W. Keller, and W. Lang, HSG-IMIT: Hahn-Schickard-Gesellschaft, Institut für Mikro- und Informationstechnik, Wilhelm-Schickard-Str. 10, 78052 Villingen-Schwenningen, Germany

For applications in micromachined switching sensors such as position and force or pressure switches, gold-based contact metallizations were manufactured and tested. The examined parameters included stability of metallization, contact resistance, and achievable lifetime as well as mechanisms of degradation. An isogeneous contact system of 300 nm TiW and 1 μm Au resulted in 10 m Ω contact resistance along with a lifetime of some 10^6 load cycles at 10 V, 10 mA.

We have manufactured micromachined switching devices, basically consisting of a silicon membrane anodically bonded on a pyrex baseplate, thereby enclosing a tightly closed cavity. Both membrane and substrate were metallized with a gold-based contact system. Preliminary tests had been run to gather data on the required switching distances for various electrical loads in the range of 5 ... 300 V, 1 ... 500 mA which also yielded a strong influence of the metallization system on the speed of contact degradation.

As a promising metallization system, we have therefore employed 1 μm of gold on 300 nm TiW. These devices were characterized in virgin state and in intervals after ageing in lifetime tests.

Four-point measurements on the switch resistance yielded values of 10 m Ω of a single pair of contacts; the achievable lifetime is limited by contact erosion and therefore depends on the available contact area. Since for membrane switches this area is determined by membrane load, the measured lifetime of some 10^6 load cycles at 10 V, 10 mA constitutes just a low limit for lifetime.

H-II.2 11:10-11:30

MICROMACHINED CHEMICAL REACTION SYSTEM, M. Koch, C.G.J. Schabmueller, A.G.R. Evans, A. Brunnschweiler, Department of Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, UK

This report presents a micromachined chemical reaction system which is based on the integration of several microfluidic devices. The system is realised by anodically bonding two pumps, two flowsensors and a micro-mixer on top of a micromachined fluidic circuit board.

Such a microfluidic chemical reaction system could be employed in a variety of applications. These are: Measurement of the reaction gradient (stopped flow), screening of chemicals for drug discovery or DNA synthesis, enzyme & substrate reactions, high temperature as well as light induced reactions (Diels-Alder reactions or cyclo additions).

Compared with conventional reactions several advantages are gained with a shift to microsystems: Clean reactions are possible due to constant flushing out of the products, a very homogeneous temperature distribution is achievable for endothermic reactions. Furthermore, reactions are safer through the use of small quantities. With the use of massive parallelisation of these systems the same volumes could be processed as with larger systems.

The used micropumps are membrane pumps with piezoelectric actuation. The pumping rates are from 0 to 150 $\mu\text{l}/\text{min}$. Both flowsensors are based on the temperature difference method. Three bridges are placed in the flow channel with a heater in the center and temperature sensors upstream and downstream. The principle of the mixing/reacting chamber used for this system is diffusion because of the small value of the Reynold's number in micro-capillaries. Two fluids/chemicals come together through laterally alternated inlets in order to increase the boundary surface between them.

The whole system is functional and leakage through the joints does not occur. The results for the reaction system will be presented at the conference.

SYMPOSIUM H

H-II.3 11:30-11:50

PYROTECHNIC ACTUATOR: A NEW GENERATION OF Si INTEGRATED ACTUATOR, C. Rossi, D. Estève, LAAS-CNRS, 7 ave. du colonel Roche, 31077 Toulouse cedex 4, France

Mechanical micro actuators on silicon play a major role in the development of microsystems. In this context, many developments have been performed on electrostatic, piezo electric or pneumatic actuators. However, limitations remain when energetic micro actuations have to be created. We propose in this paper, a new original type of actuation based on the force generated by the combustion of a solid propellant. It consists of micro-machined silicon microheater (3mmx3mmx0.3mm) where is deposited a thin film of propellant (2mmx2mmx0.2mm). Its functioning principle is based on the hot gas emitted by the auto combustion of the propellant when its temperature reaches 300°C locally.

In this paper, we present the characteristics and performances of a pyrotechnic actuator. A thermal modelling and a technological study enable us to fabricate a silicon microheater with very good performances in terms of thermal yield and fabrication yield. Theoretical and experimental studies on the combustion of small quantities of propellant conclude the feasibility of pyrotechnic actuators. Results gives an ignition energy of 9mJ/mm² and combustion characteristics depending on the confinement. When thermal losses are null, the combustion rate is 2.3mm/s, the pressure is 0.22MPa and the temperature is 647°C. The over pressure generated by the propellant combustion ranges from a few mBar to several tens Bar.

We conclude by presenting two examples of application for pyrotechnic actuator: a one shot micro valve and a gas generator.

H-II.4 11:50-12:10

ELECTROSTATICALLY ACTUATED MICROMIRROR DEVICES IN SILICON TECHNOLOGY, W. Lang, H. Pavlicek, Th. Marx, H. Scheithauer, B. Schmidt, HSG-IMIT, Hahn-Schickard-Gesellschaft, Institut für Mikro- und Informationstechnik, Wilhelm-Schickard-Str. 10, 78052 Villingen-Schwenningen, Germany

Micromirrors with a size of 1mm to 3mm for laser beam deflection are described. The mirrors are fabricated from single crystalline silicon using bulk micromachining and are actuated electrostatically.

Mirrors used for laser beam deflection must have a comparatively large size (1 mm sidelength or more) and very good surface quality. For that reason, surface micromachining of deposited films is not applicable. We developed a process to structure the mirrors in bulk silicon, the mirror surface is the polished wafer surface. The mirrors are suspended by 4µm x 10µm beams of monocrystalline silicon structured by dry etching technology. They are placed on a counterelectrode at 110µm distance using anodic bonding. A deflection of 7° is measured using an actuation voltage of 175V with static actuation. Resonant actuation at 80 Hz yields a deflection of 5.5° with 25V actuating voltage.

12:10-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III - Characterization

- H-III.1** 14:00-14:40 -Invited- **EVALUATION OF MECHANICAL MATERIALS PROPERTIES BY MEANS OF SURFACE MICROMACHINED STRUCTURES, J.Å. Schweitz** and F. Ericson, Uppsala University, The Ångström Laboratory, Department of Materials Science, Box 534, 751 21 Uppsala, Sweden
- For all micromechanical devices, mechanical properties such as elasticity constants, internal stresses, fracture limits and, for ductile materials, yield limits and strain-hardening behaviour, are of paramount importance in design and use. Furthermore, mechanical integrity aspects are important also for devices with non-mechanical functions. During the last two decades, a diversified and somewhat scrubby flora of methods, instrumentation and microstructures for mechanical microcharacterisation has evolved. Early results were difficult to reproduce and verify, but lately an increasing degree of agreement between reported results is discernible. This paper reviews some recent development of techniques using surface micromachined structures, with special emphasis on stress-strain, internal stress, and fracture property characterisation of brittle and ductile materials. Particular attention is given to evaluation issues such as analytical and numerical modelling (FEA), identification and elimination of error sources, and proper statistical treatment of the results (such as Weibull analysis of fracture results).
- H-III.2** 14:40-15:00 **DETERMINATION OF MICROMECHANICAL PROPERTIES OF THIN FILMS BY BEAM BENDING MEASUREMENTS WITH AN ATOMIC FORCE MICROSCOPE, C. Serre, A. Pérez-Rodríguez, J.R. Morante, Dept. Electrònica, Universitat de Barcelona, Spain, P. Gorostiza, Serveis Científico-Tècnics, Universitat de Barcelona, Spain, J. Esteve, CNM-CSIC, Campus UAB, Bellaterra, Spain**
- The miniaturisation of microelectronic devices which is reaching the mechanical field, requires accurate methods to test and evaluate the mechanical properties of the used films or microstructures. In general, these properties will strongly depend on their fabrication process, so that a systematic characterisation is required for each individual layer in order to optimise the design of micromechanical structures. Accurate measurements of these parameters can only be achieved by miniaturising the test probe to a size approaching the film thickness and the microstructures dimensions.
- In this work, mechanical measurements performed with a novel beam bending based method using an atomic force microscope (AFM) in contact mode are presented. This method, which does not need any vacuum chamber, combines a very high load resolution with a nanometric precision in the measurement of the cantilever deflection. Moreover, once the system has been calibrated, measurements can be performed very quickly and easily. It has been applied to the determination of the Young's modulus of micromachined polysilicon and ultra thin β -SiC cantilever beams.
- H-III.3** 15:00-15:20 **EFFECT OF SURFACE STRUCTURING ON ADHERENCE OF ANIMAL CELLS ON SILICON, S.C. Bayliss, L.D. Buckberry, P.J. Harris, I. Fletcher, *M. Tobin, Solid State Research Centre, De Montfort University, Leicester LE1 9BH, UK, *Daresbury Laboratory SRS, Warrington WA4 4AD, UK**
- Cells have been cultured directly on a range of micro- and nanostructured and bulk silicon surfaces. Nanocrystalline, nanoporous, microstructured and bulk amorphous and crystalline surfaces have been investigated. A range of cell types have been grown, representing possible end-uses in bioapplications. We have investigated the subsequent viability of the cells using a range of techniques specially adapted for opaque substrates. Images of the interface region have been obtained using confocal microscopy. It has been shown that different cell types prefer different surfaces, both in shape and size. Furthermore, we find from microscopy and XAFS that, as is to be expected, the surface pre-processing is also important.
- The lack of cytotoxicity of Si surfaces needs to be confirmed if these materials are to be accepted as truly bio-compatible. These preliminary studies indicate however that structured silicon offer distinct advantages over bulk silicon surfaces for cell adherence and growth since they do not require coating with substances such as polylysine to support cell growth. Furthermore such surfaces can be applied to most object geometries. Possibly most importantly, nanostructured silicon is light addressable, giving rise to speculation for sensors and intelligent implants for in vitro and ultimately in vivo applications.
- H-III.4** 15:20-15:40 **CHARACTERIZATION AND MODELING OF A CMOS COMPATIBLE MEMS TECHNOLOGY, L. Latorre, P. Nouet, Y. Bertrand, LIRMM, Montpellier, France; P. Hazard, Schneider Electric, Nanterre, France and F. Presseccq, CNES, Quality Assurance Delegation, Toulouse, France**
- In this paper we discuss the use of test structures to characterize a microsystem technology. Using simple devices and elementary mechanical relations, we determine the properties of sensor parts, i.e. the piezoresistive factor of polysilicon and a complete set of electro-mechanical relations that can be used for the design of Microsystems. Using a CMOS wafer with electronic parts on it, several techniques can be used to implement sensors. Front-Side Bulk Micromachining (FSBM) can be associated or not with Back-Side Bulk Micromachining (BSBM) and Sacrificial layer techniques. Extra layers can also be added to a processed wafer to implement sensor parts. As the cost of the post-process is strongly affected by the needs for alignment, FSBM seems to be a very promising technique due to its self-alignment capability. However, a CMOS VLSI technology is neither characterized nor optimized for its electro-mechanical properties. In order to do this characterization, we present in this paper a minimum set of test structures together with associated mechanical relationships. This make it possible to describe the mechanical behavior of the sensing device and simulate the sensor as a resistance in an electronic design. Analog HDL model of simple structures such as cantilever beams, clamped bridges and so on, has been derived and experimentally validated.

H-III.5 15:40-16:00

DYNAMIC DETERMINATION OF YOUNG'S MODULUS OF ELECTROPLATED NICKEL USED IN LIGA TECHNIQUE, H. Majjad, LMARC & LPMO, S. Basrour, LPMO, 32 av. de l'Observatoire 25044 Besançon, France, P. Delobelle LMARC, 24 rue de l'Épitaphe 25000 Besançon, France

Mechanical properties of materials involved in the fabrication of new microactuators must be well characterized in order to be used in CAD and the simulation of Microsystems. In this way, we report a study of the Young's modulus E of electroplated Nickel used in the LIGA (Lithography Galvanoformung Abformung) technique. This mechanical parameter was obtained by the analysis of vibration frequencies of free-clamped microcantilevers. The resonant frequencies of in-plane and out-of-plane flexural modes were measured with an optical bench. The experimental results are compared to the frequencies derived from a pure elastic finite element model. The variation of the boundary conditions, in particular the description of the clamped part of the devices, allows for good agreement between the experimental and the simulation. The correlation between these two methods leads to the determination of the Young's modulus of Nickel. First results lead to an average value of 185 GPa which is lower than the data reported for the bulk material. These results are in good agreement with our previous values obtained by steady-state bending tests and other works reported in the literature. E is insensitive to the direction of the excited mode which is characteristic of an isotropic behavior of the electroplated metal.

16:00-16:40

BREAK

SESSION IV - Porous Silicon I

H-IV.1 16:40-17:00

THICK OXIDISED POROUS SILICON LAYERS FOR DESIGN OF A BIOMEDICAL THERMAL CONDUCTIVITY MICROSENSOR, V. Lysenko, Ph. Roussel, B. Remaki, G. Delhomme, A. Dittmar, D. Barbier, Laboratoire de Physique de la Matière, INSA de Lyon, CNRS UMR 5511, Av. Albert Einstein, Bât. 502, 69621 Villeurbanne Cedex, France

Porous silicon (PS) offers new possibilities to be applied as thermal insulating material for microsensor design due to its low thermal conductivity (TC) value (0.5 - 4.5 W/m K). A biomedical TC microsensor based on differential thermoelectric measurements has been designed using a PS substrate. In order to ensure an efficient thermal isolation in the microsensor, main thermal and geometrical characteristics of the PS layers as well as of the whole microsensor have been numerically simulated.

PS layers with low TC have to be thick and mechanically stable under further processing. To form thick (50 - 200 μm) and stable PS layers, a new approach based on progressive changing of anodisation current density (from 100 to 25 mA/cm²) during PS formation has been elaborated. To find a suitable compromise between low TC and mechanical stability of thick PS layers, a new thermal oxidation recipe at moderate temperatures (500 - 700 °C) in dry oxygen atmosphere has been applied. It leads to 20% - 50% oxidation fraction in PS layers (measured by Energy Dispersive Spectroscopy) corresponding to TC values of 2.6 - 1.8 W/m K, respectively.

Smooth surface state of the PS layers ensured by the choice of a PS formation mode and a specific oxidation procedure has been characterised by means of atomic force microscopy.

H-IV.2 17:00-17:20

POROUS SILICON TECHNIQUE FOR REALIZATION OF SURFACE MICRO MACHINED SILICON STRUCTURES WITH LARGE SUBSTRATE GAP, H. Artmann, Robert Bosch GmbH, Department FV/FLD, P.O.Box 10 60 50, 70049 Stuttgart, Germany

Electrochemical etching with hydrofluoric acid generates a porous silicon layer underneath a surface micro machined silicon structure. The obtained porous layer thickness can be bigger than 50 μm . Due to the large inner surface the porous silicon layer can be etched selectively acting as a sacrificial layer.

A further method to realize large gaps is direct etching of silicon by electropolishing.

Both methods were used to increase the gap between free standing structures and bulk silicon.

The large gap reduces the air damping and leads to an increase of the Q-factor to obtain high-Q resonators. The influence of gap size and pressure on the Q-factor was experimentally investigated with laterally oscillating planar microstructures. The results will be compared to theoretical calculations and discussed with respect to conventional sacrificial layer techniques.

H-IV.3 17:20-17:40

SINGLE STEP ELECTROCHEMICAL ETCHING IN AMMONIUM FLUORIDE, H. Ohji and P.J. French, Delft University of Technology, Postbus 5031, 2600 GA Delft, The Netherlands

This paper presents a new etch technique for micromachining using ammonium fluoride etchant. Electrochemical etching in hydrofluoric acid is known as a technique of porous silicon formation. This technique has been applied to fabricate 3-D structures in single crystal silicon [1]. When aluminium is used in a sensor as an interconnect layer, it is difficult to apply this etching to fabricate mechanical structures. Because the aluminium is attacked by the hydrogen ion during the etching. To solve this problem, ammonium fluoride is used as an etchant. Experimental set-up and process flow are as follows. Start material was n-type (100) silicon. Positive voltage was applied between the sample and the counter electrode. The back side of the sample was illuminated by white light to generate electronic holes. Silicon nitride was deposited on top of the surface and patterned to make initial pit by KOH[2]. Vertical walls were formed by electrochemical etching in anisotropic mode. After the desired depth was obtained, current density was increased by adjusting the light to enlarge the width of the trenches. This results in the trenches being connected under the structures in isotropic mode. Thus free standing structures made of single crystal silicon were obtained. The etch rate and the morphology of the etched surface are investigated for etch parameters. Optimization of the etch parameters makes it possible to fabricate free standing structures without aluminium being damaged.

[1] H. Ohji, P.J. Trimp and P.J. French, Proc. MEMS98 workshop (1998)246.

[2] V. Lehmann and H. Foll, J.Electrochem. Soc., 137(1990)653.

H-IV.4 17:40-18:00

BREAKING THE ISOTROPY OF POROUS SILICON FORMATION BY ELECTRICAL FIELD-GUIDANCE, A. Zeitschel, A. Friedberger, W. Welser, G. Müller, Daimler Benz AG, Forschung und Technologie FT2/M, PO Box 80 04 65, 81663 Munich, Germany

In the past there have been a number of publications about using porous silicon as a sacrificial layer for micro-machining. Because porous silicon formation is an inherently isotropic process, the fabrication of bulk Si structures with large lateral extent has so far been impossible. In the present paper we report on a method that allows the etch front to be guided along non-uniform electrical field profiles within the Si wafers to be micro-machined. As an application example we demonstrate thermally isolated silicon membranes (hot plates) to be used as low-power consumption heaters for gas sensitive materials.

To this end lateral and vertical doping profiles have been produced in the front and backside surfaces of p-type Si wafers by means of P ion implantation. In this way non-uniform electrical field profiles were generated that forced porous silicon formation to proceed laterally underneath large n-type doped bulk Si surface layers. While conventional porous silicon processes only allowed for the underetching of structures with lateral dimensions about twice the wafer thickness, the novel anisotropic process allowed free-standing structures to be formed with lateral dimensions ranging up to ten times the wafer thickness.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

POSTER SESSION

14:00-16:00

See programme of this poster session p. H-17 to p. H-21.

16:00-16:20

BREAK

SESSION V - Biological and Chemical Devices

H-V.1 16:20-17:00 -Invited-

MICROSTRUCTURING OF ORGANIC LAYERS FOR MICROSYSTEMS, G. Urban, Albert-Ludwigs-University Freiburg, Am Flugplatz, 79085 Freiburg, Germany

Photopatterning of organic photoresist is the standard tool for microstructuring in microelectronics. Therefore it is not surprising that in the field of micro- and nanosystem technology such a technique is also preferred for mass production. The top-down approach for getting microstructures in microsystems comprises different photoresists for UV-, X-ray-, e-beam and ion projection lithography. Problems are the demands for high aspect ratios and depth of focus. This can be solved by new lithographic tools or conformal resists. To get functionalized structured surfaces photopatterned organic layers as membranes or nanolayers were also used. Hydrophobic and hydrophilic domains can be realized, also enzymes, receptors and antibodies immobilized in photostructured membranes. In such a way biocompatible surfaces can be realized and also sensor surfaces for analytical purposes. Miniaturized biosensors comprising the enzymes glucose oxidase are now the sensors with the largest impact and importance worldwide. The bottom-up approach for nanosystem technology also uses photostructuring methods for defined immobilization or deposition of supramolecular moieties to create defined surfaces. However other techniques as nanoplotting, nanodispersing and embossing techniques may be used for deposition and immobilization of organic molecules. Affinity assays, cell assays and DNA devices on chip can be realized for rapid screening purposes in future.

H-V.2 17:00-17:20

INTEGRATION OF A SENSITIVE MATERIAL TO A SILICON BASED DEVICE FOR CO DETECTION, O. Renault, D. Briand, G. Delabouglise, J.F. Currie* and M. Labeau, LMGP/INPG, BP46, 38402 Saint Martin d'Hères, France, and * LISA/EPM, P.O. Box 6079, Montréal, H3C3A7, Canada

A sensitive semi-conductor oxide has been successfully integrated to a silicon based prototype of sensor for environment pollution as CO.

The sensitive material SnO_2 includes catalyst Pd aggregates and provides a low temperature detection (80-120°C) by conductance change (sensitivity $S = (G - G_0)/G_0 = 20$ at 100°C for 50 ppm CO in air).

The <100> silicon substrate, coated by a Si_3N_4 insulating film, includes a micro-heater, a temperature measuring resistor, and Pt interdigital electrodes covered with the sensitive material. The integration is performed using an aerosol-CVD process at atmospheric pressure which provides flexible and well controlled polycrystalline sensitive films: 10-15 nm grain size, 2-4 nm metallic aggregate size.

It has been demonstrated the excellent compatibility of the sensitive material with the Si_3N_4 undercoat, compared with the more commonly used SiO_2 one. The role of the Pt electrode and of its interface with the sensitive material has been studied.

The operating cycle of the system has been studied regarding to the necessity of reactivating the sensitive material at regular intervals by heating at higher temperature.

H-V.3 17:20-17:40

OZONE DETECTION USING LOW-POWER-CONSUMPTION METAL-OXIDE GAS SENSORS, Th. Becker, L. Tomasi, Chr. Bosch-v.Braunmühl, G. Müller, Daimler Benz AG, Forschung und Technologie FT2/M, PO Box 80 04 65, 81663 Munich, Germany; G. Sberveglieri, G. Faglia, E. Comini, Dept. of Chemistry and Physics of Materials, University of Brescia, Brescia, Italy

Thin films of RGTO- SnO_2 deposited on micromachined heater elements were characterized for their sensitivity towards prominent air pollutants such as O_3 , NO_2 , NO and CO. Whereas previous work has mainly concentrated on detecting reducing agents such as CO, our recent work has clearly revealed that such thin films mainly respond to O_3 . At normal operating temperatures of the order of 400°C, environmentally relevant concentrations of O_3 (< 40 ppb) were easily detected with response and recovery times of the order of a few min. Upon reducing the surface temperature of the SnO_2 films this ozone sensitivity persists almost down to room temperature, thus opening the perspective of fabricating extremely low-power-consumption gas sensors. In this contribution our recent results on the ozone sensitivity of RGTO- SnO_2 films are compared and contrasted to similar results obtained in CO and NO_x detection experiments. The problem of detecting ozone in the presence of small concentrations of CO, NO_x and various humidity background levels are discussed.

H-V.4 17:40-18:00

INVESTIGATION OF THE MIS GAS-SENSITIVE STRUCTURES WITH Pd AND Pd/Cu METAL LAYERS, V.G. Litovchenko, T.I. Gorbanyuk, A.A. Efremov, A.A. Evtukh, I.P. Lisovskii, Institute of Semiconductor Physics, 45 Prospekt Nauki, Kiev 252650, Ukraine

Investigation of MIS structures with Pd and Pd/Cu metal layers have been performed and experimental characteristics of MIS structures, as a hydrogen-gas sensors, have been compared. The metal films were deposited by magnetron sputtering in Ar plasma. Pd layer thickness was in range 20-60 nm. In case of Pd/Cu film the ultrathin layer of Cu was deposited on Pd. The measurements of capacitance-voltage characteristic shifts (ΔV_{fb}) have been performed. The kinetics of ΔV_{fb} changing with time have been measured too. To investigate the ageing processes the annealing at temperatures 100-200°C during 0.3-3 hours have been made. Influence of air, oxygen and humidity on transient characteristics of MIS hydrogen sensitivity structure have been studied in detail.

The results can be summarized as follows: - initial sensitivity to hydrogen is higher for MIS structures with Pd/Cu electrodes; - annealing at temperature 150°C increases the sensitivity to hydrogen, in case of Pd MIS the decrease is observed (about 20%); - annealing at 200°C and higher decreases the signal both for Pd and for Pd/Cu MIS structures; - treatments at temperatures above 200°C retard the transient signal growth in all cases, i.e. the samples are aged. The model for explanation of the experimental results have been proposed

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VI - Deposition and Preparation

- H-VI.1** 8:30-8:50 PHOTOPOLYMERIZATION BY EVANESCENT WAVES: A NEW METHOD TO OBTAIN NANOMETRIC FILMS OF PHOTOPOLYMER, A. Espanet, C. Ecoffet and D.J. Loughnot Laboratoire de Photochimie Générale, CNRS-UMR7525, 3 rue Alfred Werner, 68093 Mulhouse, France
(WITHDRAWN)
- H-VI.2** 8:50-9:10 PERMALLOY ELECTROPLATING THROUGH LITHOGRAPHIC MASK, J.M. Quemper, S. Nicolas, J.P. Gilles, J.P. Grandchamp, A. Bosseboeuf, T. Bourouina, E. Dufour-Gergam, Institut d'Electronique Fondamentale, Bât 220, 91405 Orsay, France
Electrodeposited magnetic Ni-Fe films are used in storage devices and become usually used for MEMS. In this paper we present some fundamental results related to this material concerning the influence of the electrodeposition conditions on the film composition and uniformity.
A preliminary permalloy electrodeposition study has been achieved on copper evaporated films without resist patterns. The growth rate varies linearly versus the current density (typically 50nm/min for 10 mA/cm²). The electrolyte stirring influences the growth rate too, introducing a reduction of this one and a threshold. This is due to the competition between deposition and etching. Concerning the influence of deposition parameters on alloy composition, we observe the well known anomalous deposition: the less noble metal (Fe) deposits preferentially to the noble metal Ni. The composition is constant for films from 100 to 1000nm film thickness and the Fe percentage decreases with the current density. An alloy Ni₈₀Fe₂₀ is obtained for a density of 12.5mA/cm². We also present the influence of the stirring effect. The lowest roughness is obtained for the highest thickness because an important hydrogen desorption is produced at the beginning of the growth, and the bulk value of massic density is found in the case of permalloy stoichiometry. The magnetic characteristics are determined with a vibration magnetometer. Good magnetic properties are obtained (coercivity = 0.35 Oe for a thickness of 600nm).
In a second part, the growth through lithographic mask is studied. The composition is analysed for a same aperture value and several resist thicknesses to characterize the convection limitation. The uniformity of the composition is determined as a fonction of the size of the resist aperture, the cathode position and the current density.
- H-VI.3** 9:10-9:30 MICROMACHING OF AN AIR-BRIDGE STRUCTURE USING THIN-FILMS ON GLASS SUBSTRATES, M. Boucinha, V. Chu, INESC, Lisboa, Portugal, and J.P. Conde, Department of Materials Engineering, Instituto Superior Técnico, Lisboa, Portugal
MEMS, sensors and actuators and microstructures processed on crystalline silicon wafers are a fast developing field. For some applications, namely those which require large areas, it is important to develop thin-film materials and processes that are compatible with large area substrates such as glass, plastic or steel.
In this paper, we describe in detail the processing and microstructuring of an air-bridge structure on Corning 7059 glass. The air-bridge structure consists of a gate and of a bridge suspended over the gate separated by a gap. Gate and bridge materials used are hydrogenated amorphous silicon, microcrystalline silicon or a metal. The maximum processing temperature was 300°C. In our structure the bridge height is 5000 Å and the bridge span is between 10 and 20 µm.
The application of these structures to a variety of novel devices will be discussed.
- H-VI.4** 9:30-9:50 FORMULATION OF STABLE SILVER-ON-POLYIMIDE INTERFACE BY CHEMICAL METALLIZATION, A. Syzdykova, S. Kudaikulova, G. Boiko, B. Zhubanov, M. Buranbaev*, G. Atanbekova*, K. Zhumanov*, Institute of Chemical Sciences, 106 Valihanov, Alma-Ata, Kazakstan, *Physical Department of Kazak State University, 96 Tolebi, Alma-Ata, Kazakstan
The possibilities of heterogeneous chemical modification allow to formulate stable silver interface on polyimide (PI) films. Metallization process consists of three main steps: hydrolysis of the film, chelating by metal cations and reduction.
The first step provides deepness of metal incorporation into the film and size of nanopores. Chelating step with regulated reverse diffusion of cations to the surface of the film allows to formulate size of reduced nanoparticles. Conduction of reduction of Ag⁺/PI film by NaBH₄ and organic reducing agents has shown that the most stable coating is obtained by the first one. Metallization quality was investigated by measurement of electroconductivity and reflection of the surface of incident light at 74° in the region 300-700 nm. Reflectivity of optical mirror was taken as 100%. These results has shown that the most qualitative interface is formulated with the use of reverse diffusion method. Electroconductivity of the films obtained by reverse diffusion was 10⁴ S/cm, optical reflection(R - 80%), and size of Ag nanoparticles determined by X-ray diffractometry was d=13 nm. The same characteristics of the films obtained by usual method were as follows: nonconductivity, R-30%, d - 5-8 nm.

SYMPOSIUM H

H-VI.5 9:50-10:10

PECVD SILICON OXYNITRIDE OPTIMIZED FOR APPLICATION IN INTEGRATED OPTICS, K. Wörhoff, A. Driessen, P.V. Lambeck, H. Albers, L.T.H. Hilderink, and Th.J.A. Popma, MESA Research Laboratory, University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands

Within the last years, CVD grown silicon oxynitride (SiON) became increasingly important for the realization of low-cost, compact integrated optics devices. The major advantage of SiON is given by the tunability of the refractive index over a wide range ($n = 1.45-2$) resulting in a large degree of freedom in integrated optics design.

Plasma Enhanced (PE) CVD SiON layers are grown from SiH_4 , N_2 , NH_3 and N_2O in a parallel plate reactor. The process has been optimized with respect to deposition of layer with high uniformity in layer thickness ($\delta d < 1\%$) and refractive index ($\Delta n = 2-7 \times 10^{-4}$) and excellent reproducibility of the layer parameters. The optical loss of as-deposited slab-type waveguides has been determined to be as low as 0.2 dB/cm at 632.8 nm wavelength. Due to absorption of N-H and Si-H vibrational overtones, the optical loss at 1550 nm is increased, e.g. 0.5 dB/cm for low index layers. By annealing, the hydrogen content can be reduced as is confirmed by IR-spectroscopy and ERDA.

Based on PECVD technology, a layer structure fulfilling the strong requirements of telecommunication devices, has been designed for operation at 1550 nm wavelength. This structure, consisting of a SiON core layer ($n=1.4857$) surrounded by thick oxide cladding layers ($n=1.4637$), has the potential for realization of low-loss waveguides with a small bending radius and high fiber-to-chip coupling efficiency.

10:10-10:50

BREAK

SESSION VII - Etching

H-VII.1 10:50-11:10

RECENT ADVANCES IN Si ETCHING FOR MEMS USING THE ASETM PROCESS, H. Ashraf, J.K. Bhardwaj, J. Hopkins, A.M. Hynes, I. Johnston, J.N. Shepherd, Surface Technology Systems Ltd, Imperial Park, Newport, NP1 9UJ, UK

In the ongoing enhancement of MEMS applications, the STS Advanced Silicon Etch, ASETM, process satisfies the demanding requirements of the industry. Typically, highly anisotropic, high aspect ratios profiles with fine CD control are required. Selectivities to photoresist of 150:1 with Si etch rates of up to 7 $\mu\text{m}/\text{min}$ are demonstrated. Applications range from shallow etched optical devices to through wafer membrane etches. This paper details some of the fundamental trends of the ASETM process and goes on to discuss how the process has been enhanced to meet product specifications. Parameter ramping is a powerful technique used to achieve the often conflicting requirements of high etch rate with good profile/CD control. The results are presented in this paper.

H-VII.2 11:10-11:30

ROUGHENING AND SMOOTHING DYNAMICS DURING KOH SILICON ETCHING, R. Divan, N. Moldovan, Institute of Microtechnology Bucharest, PO Box 38-160, Romania and H. Camon, LAAS/CNRS 7 Avenue du Colonel-Roche, 31077 Toulouse Cedex, France

We studied the influence of surface preparation prior to KOH etching and of surfactants added to the etchant over the etching rates and roughness of the Si (111) and Si (100) surfaces. The investigated etchants were 20%KOH at 80°C, and 25%KOH with small amounts of anionic, cationic and non-ionic surfactants. The surface preparation refers to the use of the following solutions for the native oxide removal: $\text{HF}:\text{H}_2\text{O}$ 1:10 (followed by DI water rinsing and drying), $\text{HF}:\text{C}_2\text{H}_5\text{OH}$ 1:10 (dried without any further rinsing), and 10% HCl in $\text{HF}:\text{H}_2\text{O}$ 1:1 (also dried without rinsing). The first solution leaves the silicon surface saturated by hydrogen atoms, the second – mainly by fluorine atoms while the third – by hydrogen, but this time, the metallic contaminants from the HF solution are removed. The evaluations were made by mechanical profilometry and AFM. No difference between the samples dipped in HF-water and HF-alcohol could be observed. The etching rate of the samples dipped in HCl-containing solutions were almost double, while their roughness was diminished. The etch rates increased when using surfactants: about 7% for the cationic-, 12% for the anionic- and 20% for the nonionic-surfactants. The saturation value of the roughness was reduced from 1132 Å (rms) in the case without surfactants to 872 Å (cationic), 745 Å (anionic) and respectively 428 Å (nonionic). Tentative explanations for the roughening mechanisms are proposed

H-VII.3 11:30-11:50

3D ELECTROFORMING OR ETCHING USING UV GRAY-TONE LITHOGRAPHY, S. Nicolas, J.M. Quemper, E. Dufour-Gergam, J.P. Gilles, A. Bosseboeuf, T. Bourouina, J.P. Grandchamp, Institut d'Electronique Fondamentale, Bât 220 91405 Orsay cedex, France

Gray-tone lithography is an attractive technology to make, in a single step, non planar photoresist patterns with a complex relief, including slopes and/or curved patterns. In a second step, if the resist is not the adequate material, this technique permits the transfer of the patterns in the appropriate material by electroforming or etching.

In the first part of this paper, we present an optimized gray-tone lithography process for a AZ-4562 20 μm thick resist in order to obtain a maximum gray- level range (prebake : 90°C, 1 hour, exposure dose : 700mJ/cm² for a development time of 5 min). The gray-scale patterns are firstly drawn on a microcomputer (scale 200) and printed on a transparent film (primary mask) with a high resolution imagesetter. More than 256 totally distinct gray-levels can be obtained from white (transparent) to black (opaque) level. Then the gray-patterns are transferred onto a secondary mask (Kodak film plate) by photoreduction of a factor 20. Finally the 3D patterns are transferred into the photoresist with a 10x reduction stepper. The transmission of the primary and secondary masks as also the resist transmission have been determinate for different thermal treatments in order to simulate the whole lithographic process.

In the second part the resist patterns have been used :

- as molds for copper electrodeposition in order to study the growth mechanisms through tapered apertures which depend on current density (10- 80 mA/cm²) and mold aperture geometry.
- as mask for silicon ion beam etching. Influences of the etch selectivity, ion beam incidence angle and ion energy on pattern deformations and surface roughness have been investigated.

SYMPOSIUM H

H-VII.4 11:50-12:10

SILICON ELASTOMER AS PROTECTIVE LAYER IN 3D MICROFABRICATION OF MOEMS, P. Obreja, R. Muller, E. Manea, National Institute for Research and Development in Microtechnologies, PO Box.36-160, 72225 Bucharest, Romania

The paper presents silicon anisotropy etching experiments in KOH and TMAH solutions in different conditions, using an organic silicon compound as protective layer for the front side of the wafer.

The starting material was a 460* μ m thick, <100> oriented n type silicon wafer. On the front side can be made structures by IC standard technology.

The last process in 3D microfabrication of micro-opto-electo-mechanical systems (MOEMS) is anisotropic etching. For the protection of front side of the wafer usually Si_3N_4 and SiO_2 are used. Si_3N_4 is difficult to be removed in the lithographic process sequence and thermal SiO_2 present strong compressive stress and can be used only in special conditions (shorter time required and lower etching concentrations).

The proposed protective layer is a silicon elastomer that provided good adhesion and masking properties and was tested for the manufacturing of thin silicon membranes, using bulk micromachining.

The experiments were performed in 10 % TMAH and 10% TMAH : H_2O_2 aqua solutions at 85°C and KOH (20% and 40%) at 80°C.

So, the thin silicon membranes with <10 μ m thickness have been obtained. The organic layer assures the protection during etching process and can be chemically removed after this procedure.

12:10-14:00

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION VIII - Bonding and Packaging

H-VIII.1 14:00-14:40 -Invited-

WAFER BONDING FOR MICROSYSTEMS TECHNOLOGIES, U. Goesele, A. Schumacher, G. Kraeuter, K. Gutjahr, M. Reiche, A. Ploessl, and P. Kopperschmidt, Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany and Q.Y. Tong, T.H. Lee, Y.L. Chao, L.J. Huang, and W.J. Kim, Wafer Bonding Laboratory, School of Engineering, Duke University, Durham NC 27708, USA

In microsystems technologies frequently complex structures consisting of structured or plain silicon or other wafers have to be joined to one mechanically stable materials structure. The different parts should have as close as possible coefficients of thermal expansion. The "glue" to join the various parts ideally should allow a vacuum tight connection and should not introduce any contaminants (such as e.g. sodium) which would interfere with potential microelectronic components integrated on the same chip. In the future, it will increasingly of importance that the temperature to fabricate a permanent connection should be so low that the devices and the metallization on pre-processed wafers will not be disturbed. This requires joining temperatures below about 450 degree centigrades. Presently, the joining technology used in industry is still mainly anodic bonding which involves the use of a glass and temperatures around 500 degrees centigrades.

The present paper will deal with the alternative approach of "direct bonding" (also termed "fusion bonding") which has been well developed especially for silicon either covered with oxide layers or without such layers. Concepts for avoiding particle and gas related bubbles will be described. A detailed understanding of the reactions at the bonding interface will be presented which allowed the development of low-temperature bonding procedures based on plasma treatments or vacuum joining. For practical applications, a low vacuum approach allowing tight bonding at 150 degrees centigrade is of special interest. New technologies as hydrogen-implantation based "smart-cut" and "smarter-cut" thinning approaches will be mentioned as well as an extension of wafer bonding to other materials such as sapphire, GaAs and ferroelectric films.

H-VIII.2 14:40-15:00

β -SiC ON SiO_2 FORMED BY ION IMPLANTATION AND BONDING FOR MICRO-MECHANICS APPLICATIONS, C. Serre, A. Romano-Rodríguez, A. Pérez-Rodríguez, J.R. Morante, Dept. d'Electrónica Universitat de Barcelona, Spain; L. Fonseca, J.A. Plaza, M.C. Acero, CNM-CSIC, Campus UAB, Bellaterra, Spain

SiC is a wide bandgap material with a strong potential for high temperature and harsh environment sensors. Between the different polytypes, β -SiC is the one with most interesting electronic properties, and the synthesis of high crystalline quality β -SiC layers by ion implantation into Si has been reported [1]. However, the use of the SiC layer as the active region in high temperature and harsh environment conditions generally requires electrical and mechanical isolation between the SiC film and the Si substrate.

In this work we report the fabrication of SiC on SiO_2 structures by ion implantation and bonding. This process involves three steps: i) multiple C implant into Si, to obtain a buried β -SiC layer with sharp interfaces with the top Si and substrate regions, ii) selective oxidation of the top Si layer, and iii) bonding and etch-back of Si. This allows to obtain high crystalline quality β -SiC films on SiO_2 using processes compatible with Si IC technology, avoiding the use of expensive bulk SiC or Silicon-On-Insulator wafers. The detailed characterization of the SiC and SiO_2 layers in the structure will be reported, and test microstructures fabricated on the processed wafers such as beams and membranes will be presented.

1.- C. Serre et al, J. Electrochem. Soc. 144 (1997), 2211.

H-VIII.3 15:00-15:20

EFFECT OF CLAMPING CONDITIONS AND BUILT-IN STRESSES ON THE THERMOPNEUMATIC DEFLECTION OF SiO_2/Si MEMBRANES WITH VARIOUS GEOMETRIES, C. Malhaire, M. Le Berre, D. Fevbre, D. Barbier, P. Pinard, LPM-UMR C55 11, INSA Lyon, 20 av. Einstein, bât. 502, 69621 Villeurbanne Cedex, France

Clamping conditions and built-in stresses are known to induce deflections in microstructures such as composite membranes. The thermopneumatic behaviour of large square SiO_2/Si membranes with a side length from 3 to 7.5 mm, a Si thickness in the [7.7-26.5 μm] range and a SiO_2 thickness up to 1.5 μm , was studied by optical profilometry. Clamping conditions have been found experimentally to play a major role in built-in stress relaxation. Indeed for a 3.6 x 3.6 mm² membrane with SiO_2 and Si thicknesses of 1.46 μm and 17.5 μm respectively and an original deflection of 14.7 μm , this phenomenon has led to a deflection decrease of 30% after dicing. This tendency was confirmed by Finite Element Modelling using an optimized meshing. A 10% agreement has been found between the experimental and the simulated deflections of pre-stressed SiO_2/Si membranes. Oxidized (up to 1.5 μm) and bare Si membranes with thicknesses from 7.7 to 26.5 μm were studied under pressure in the [0-1 bar] range. Main tendencies are : for the thinnest membrane, with an original deflection of 30 μm , the oxide drastically influences the behaviour under pressure. For the thickest membrane, no influence of the oxide could be measured. In the intermediate range (about 20 μm), profilometry measurements and FEM have shown that the compressed oxide induces a larger deflection as if it acts as to decrease the membrane stiffness. Finally, FEM results have been checked experimentally for various membrane geometries and the interest of this tool for the design of packaging structures is discussed.

SYMPOSIUM H

H-VIII.4 15:20-15:40

SELECTION OF MATERIALS FOR REDUCED STRESS PACKAGING OF A MICROSYSTEM, A. Morrissey and J. Alderman, National Microelectronics Research Centre, University College, Cork, Ireland

Miniaturisation of many types of sensors and actuators has been realised by the advances in micromachining and microfabrication. This has led to a wide range of applications including microfluidic systems, where developments have resulted in much research in the area of μ TAS, used especially in analytical chemistry and chromatography. Among the main benefits of microsystem technology are its contributions to cost reduction, reliability and improved performance. However, the packaging of microsystems, especially microsensors, is one of the biggest limitations to their commercialisation as it can be the most costly part of sensor fabrication. This is because microsystems place extra demands on packaging techniques. For example, most microsystems need access to the outside world, other than electrical connection, in order to interact with the medium being measured or monitored, but yet the microsystem must be protected from the elements in this external environment and vice-versa. The latter is particularly the case in medical and food industry applications where even further constraints are placed upon the package design. To reduce costs, a microsystem may be packaged in plastic but because of TCE mismatches between different materials within the microsystem, the packaging process may generate high levels of stress which can negatively affect the system's operation and reliability. It is clear that conventional packaging approaches and materials are inapplicable to microsystems.

3D packaging techniques have great potential for microsystem integration. This paper will discuss the selection of materials applicable to the 3D packaging of any microsystem, including those containing extremely delicate micromachined structures such as membranes for micropumps and pressure sensors. FEM analysis aided in this selection, and the paper describes the most suitable materials in all aspects of microsystem packaging, viz. substrate, die attach and encapsulating materials, and a material for use in the construction of a "sensing chamber" about the active area of a sensor chip, and (in the case of a 3D assembly) between such a sensor and an upper chip which could, for example, be a micropump delivering the fluids to be analysed by the sensor electronics, with control electronics suitably packaged at lower levels in the 3D stacked assembly.

15:40-16:20

BREAK

SESSION IX - Laser Processing

H-IX.1 16:20-16:40

MULTILAYERSTRUCTURES DEPOSITED BY LASER ABLATION, D. Ghica*, C. Stanciu, V. Sandu**, M. Dinescu, IFA, NILPRD, PO Box MG-16, 76 900, Bucharest, Romania, *Institute of Optoelectronics, 76 900, Bucharest, Romania, **NIMP, PO Box MG-26, 76 900, Bucharest, Romania, and M. Balucani, V. Bondarenko, L. Franchina, G. Lamedica, and A. Ferrari, INFN Unit E6, University 'La Sapienza', Rome, Italy

TiN/Si structures were deposited on Si wafers by pulsed laser deposition technique. The highly conductive TiN films were grown on heated (100) Si substrates by laser ablation of a high purity Ti target in nitrogenreactive atmosphere. Subsequently, the Si layer was deposited by laser ablation of a Si target in vacuum (down to 10^{-6} mbar) or in low pressure inert gas.

The nitrogen gas pressure and the substrate temperature were found to strongly influence the TiN film structure and orientation. The degree of crystallinity of the Si layer grown on the TiN film was found to depend on Si/TiN collector temperature. Values below 500°C (the threshold of TiN oxidation activation) were used in the experiments. Techniques as X-ray diffraction, Fourier Transform Infrared Spectroscopy, Electron Microscopy, Spectroellipsometry have been used to characterize the deposited structures. The TiN/Si rectifying properties by electrical characterization of the structure is presented. The obtained Si/TiN/Si structure could be suitable to build Permeable Base Transistor (PBT, vertical MESFET) devices

H-IX.2 16:40-17:00

FEMTOSECOND LASER BASED TECHNOLOGY FOR FAST DEVELOPMENT OF MICROMECHANICAL DEVICES, R. Bähnisch, W. Groß and A. Menschig; Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Technische Physik, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

It is nearly impossible to put micro systems on the market which do not use typical materials, tools or process technologies established for microelectronic fabrication. Particularly for the realization of prototypes or small volume production there is a need for alternative, maskless process technologies. A promising new way is the laser based fast development of micro systems using an ultrashort pulsed (< 10 ps) laser.

We present a maskless, laser-based high precision direct-write process for flexible patterning to realize structured metallization as well as isolation trenches on micro parts. Also a new design concept for micro devices which used laser based fast development will be discussed. Various grippers for micro parts consisting of several thin ceramic plates which are piled up will be demonstrated.

Results will be shown for the direct patterning and the structured forward transfer of thin metal films (about 1 μ m, e.g. Au, AuSn, Al) on isolating substrates (e.g. glass, ceramics, semiconductors) and the direct patterning and cutting of various thin plates (about 100 ... 300 μ m, e.g. ceramics, glass, diamond). Thin glass plates in which holes are patterned by laser show good bond properties to silicon.

Of special interest is the combination of the patterning of isolation trenches without damage of the substrate and of the cutting of micro parts from the substrates within one technology step only by varying the laser power. A surface roughness well below 1 μ m at the cutted edges can be achieved.

H-IX.3 17:00-17:20

GROWTH OF PIEZOELECTRIC THIN FILMS WITH FINE GRAIN MICROSTRUCTURE BY HIGH ENERGY PULSED LASER DEPOSITION, F. Craciun, P. Verardi, M. Dinescu*, C. Galassi**, A. Costa**, CNR Istituto di Acustica "O.M. Corbino", Area di Ricerca Roma - Tor Vergata, Roma, Italy; *Institute of Atomic Physics, Bucharest, Romania, **CNR Istituto di Recerche Tecnologiche per la Ceramica, Faenza, Italy

Thin piezoelectric films of lead zirconate-titanate (PZT) were deposited by pulsed laser ablation from porous PZT targets and compared with films obtained from dense samples. The porous fine grained targets were obtained from nanosized powders synthesized by spray-drying of precursor solution and sintered at 700°C. The depositions were performed on Si (100) substrates carefully cleaned and heated in a vacuum chamber at 400°C. The same experimental setup (Nd-YAG laser, 0.3 J/pulse, 1064 nm, 10 ns, 10 Hz) and parameters (reactive O₂ atmosphere of pressure 150 mTorr, substrate temperature 370°C) were used for all the films. After deposition samples were investigated by x-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy (EDS). Similar analysis were performed on targets before and after deposition. It has been observed that the evolution of the two types of targets during deposition was very different and this aspect was reflected in differences of film morphologies. Films deposited from porous targets presented a uniform fine grained microstructure with only few particulates on surface, while films deposited from dense targets had a much rougher surface. EDS analysis shown important chemical differences between these particulates and the surrounding film.

H-IX.4 17:20-17:40

PULSED LASER DEPOSITION OF MULTILAYER TiN/Pb (Zr, Ti)O₃ FOR PIEZOELECTRIC MICRODEVICES, P. Verardi, M. Dinescu*, F. Craciun, R. Dinu*, C. Gerardi**, CNR Istituto di Acustica "O.M. Corbino", Area di Ricerca Roma - Tor Vergata, Roma, Italy; *Institute of Atomic Physics, Bucharest, Romania, **PASTIS-CNRS, Brindisi, Italy

Multilayer Pb(Zr,Ti)O₃ (PZT)/TiN/Si structures were grown by two subsequent laser ablation processes in reactive atmosphere. First, an oriented fcc TiN film was deposited by laser ablation of a Ti target in high purity nitrogen reactive gas. Subsequently, an oriented perovskite PZT film was grown by reactive ablation of a PZT target in oxygen atmosphere. Both deposition processes were conducted at quite low Si (100) substrate temperature: 300°C for TiN and 370°C for PZT, in the same experimental set-up (Nd-YAG laser, $\lambda = 1060$ nm, E/pulse 0.3 J, $\tau = 10$ ns, $f = 10$ Hz). TiN film properties were analysed by XRD, FTIR, electric measurements. After the deposition of the PZT layer, the obtained structure was characterized by XRD, SEM and SIMS techniques. Testing measurements, performed after the thermal evaporation deposition of an Al layer as top electrode on the PZT/TiN/Si structure, confirmed that they can be used as sensors transducer element. The highly conductive nitride TiN layer replaces the former Au layer used as bottom electrode. In this way the Au diffusion inside the Si substrate as well as in the deposited PZT layer is avoided, as could be observed from a comparative study of the SIMS spectra recorded for PZT/TiN/Si and PZT/Au/Si configuration.

H-IX.5 17:40-18:00

MICROMACHINING OF MAGNETIC MATERIALS, A. Kruusing*, **, S. Leppävuori**, A. Uusimäki** and B. Petretis***, *Tallinn Technical University, Ehitajate tee 5, 0026, Tallinn, Estonia, **Microelectronics and Material Physics Laboratories, EMPART research group of Infotech Oulu, University of Oulu, P.O.Box 444, 90570 Oulu, Finland, *** Institute of Physics, Savanorių 231, 2028 Vilnius, Lithuania

High-performance magnetic materials, such as ferrites and rare-earth compounds, are manufactured by powder compacting and sintering, a process, not suited for forming of millimeter-submillimeter parts needed in many miniature devices. On the other hand, there is no knowledge of sufficiently rapid and efficient deposition of layers of thickness of hundreds of micrometers up to one millimeter of these materials.

We have investigated two processes for micromachining of ceramic magnetic materials - electro discharge (EDM) and laser light machining. Work on investigation of erosive particles jet machining of these materials is going on.

The experiments were done with soft ferrites and NdFeB permanent magnet (PM) material.

The wire EDM provided best accuracy (some micrometers) and surface quality although the cutting speed of the ferrite was rather slow - about 2 $\mu\text{m}/\text{min}$. Transformer and electromagnet cores with overall dimensions down to 1 mm x 1 mm x 3 mm were successfully fabricated and used in experiments with miniature systems. Machining experiments of the same materials were also carried out with light of a pulsed 1.8 W Nd:YAG laser. Using focused beam with 50 μm waist diameter and 100 kHz pulse repetition rate, both ferrite and rare-earth PM plates of thickness of 1 mm were cut successfully, although with lower surface quality than by EDM.

The build-up of surface roughness and structural changes of NdFeB magnet during the laser machining were investigated.

Friday June 19, 1998

Vendredi 19 juin 1998

Morning

Matin

SESSION X - New Materials

H-X.1 8:30-8:50

PROPERTIES OF SiO_xN_y FILMS DEPOSITED BY LPCVD FROM $\text{SiH}_4/\text{NH}_3/\text{N}_2\text{O}$ GASEOUS MIXTURE, P. Temple-Boyer, B. Hajji, A. Martinez, LAAS-CNRS, 7 Av. du colonel Roche, 31077 Toulouse Cx 4, France, J.L. Alay and J.R. Morante, Dept. d'electronica, Facultat de Fisica, Universitat de Barcelona, Av. Diagonal 645, 08028 Barcelona, Spain

Varied silicon oxynitride SiO_xN_y films have been deposited by low pressure chemical vapor deposition (LPCVD) from silane SiH_4 , ammonia NH_3 and nitrous oxide N_2O by adjusting the $\text{NH}_3/\text{N}_2\text{O}$ gas flow ratio. SiO_xN_y stoichiometries have been characterised by X-ray photoelectron spectroscopy (XPS) and films thicknesses and refractive indexes have been measured by ellipsometry and profilometry. The different results are compared to the Bruggeman theory applied to the $\text{SiO}_2/\text{Si}_3\text{N}_4$ heterogeneous medium, demonstrating that the stoichiometry can be conveniently determined by ellipsometry.

Films residual stresses have been characterised by profilometry through wafer curvature measurements. From compressive to tensile stress values have been obtained, evidencing the existence of a no-stress oxynitride film. Such phenomena are related to the SiO_xN_y stoichiometry and explained by considering the deposition mechanisms of the $\text{SiH}_4/\text{NH}_3/\text{N}_2\text{O}$ gaseous mixture and the thermo-mechanical properties of silicon oxynitride.

H-X.2 8:50-9:10

A HIGH TEMPERATURE PRESSURE SENSOR PREPARED BY SELECTIVE DEPOSITION OF CUBIC SILICON CARBIDE ON SOI, M. Eickhoff, H. Moeller and G. Kroetz, Daimler-Benz AG Research and Technology, Dep. FT2/M, Postbox 80 04 65, 81663 Munich, Germany

β -SiC has been shown to be a very convincing material for high-temperature sensor applications, like high-temperature pressure sensors with piezoresistive SiC sensing elements. However, structuring of the SiC layer especially in selectivity to an underlying SiO_2 -layer often causes severe problems within the process. Another problem is wafer-bending due to the high tensile stress when SiC is deposited on large substrates.

In order to avoid these drawbacks we applied a selective deposition process to realize a high-temperature pressure sensor with β -SiC piezoresistors. We show the enormous simplification in processing due to this new deposition technique. The pressure sensor was characterized up to temperatures of 400°C.

H-X.3 9:10-9:30

PIEZOELECTRIC PROPERTIES OF PZT FOR MICRO-CANTILEVER, E. Cattán, T. Haccart, G. Vélú, D. Rémiens, Laboratoire des Matériaux Avancés Céramiques, Université de Valenciennes et du Hainaut-Cambrésis, ZI Champ de l'Abbesse, 59600 Maubeuge, France

The investigation of piezoelectric properties of materials in the thin layer form became an important task because of the increased range of their applications as actuators and as sensors. The sensor magnitude, which is possible for a micro-cantilever, is a direct function of the piezoelectric constant e_{31} . To date there is no reliable data on the magnitude of e_{31} for thin $\text{Pb}(\text{Zr,Ti})\text{O}_3$ films. This ferroelectric material and the modified compositions have attracted great attention in recent years as promising for use in microelectromechanical systems. So, we propose an experimental method to evaluate this constant. This last is measured only after voltage poling treatment. The values obtained are then under-estimated compared with a value measured directly during the poling treatment. A remanent piezoelectric constant of -5 C/m^2 was observed that agrees well with the values previously reported for the bulk ceramics. The efficient piezoelectric activity have been studied as function of the film orientation. The parameters as, coercitive field, saturation field, curve of first polarization, and self polarization of the remanent piezoelectric hysteresis loops was compared for PZT thin film in the range thicknesses of 0.3 to 3 μm . We will associate also the ferroelectric and dielectric results.

H-X.4 9:30-9:50

LOW TEMPERATURE CRYSTALLIZED Ti RICH NiTi SHAPE MEMORY ALLOY FILMS FOR MICROACTUATORS, J.L. Seguin, M. Bendahan, A. Isalgue*, V. Esteve**, H. Carchano and V. Torra*, Laboratoire EPCM, Case A62, Faculté des Sciences de Saint Jérôme, 13397 Marseille Cedex 20, France; *CIRG-DFA UPC, Campus Nord B4, 08034 Barcelona, Spain; **DIOC-ICD, U. Jaume I, P.O. Box 224, 12080 Castellon, Spain.

Films of NiTi shape memory alloy have the potential to be used as high performance actuating layers for micro-electromechanical systems. The shape memory effect involves a thermally induced phase transformation between a low temperature ductile phase and a high temperature high strength phase. Thus, in order to exhibit the shape memory effect, the NiTi films should have a crystalline structure, which is usually obtained by a high temperature annealing. Obtaining low temperature crystallised NiTi films would ensure a good compatibility with microelectronic process and enable deposition on substrates that cannot endure high temperatures, like polymers. We found that NiTi films containing an excess of Ti (52% at.) are crystallized when deposited on Si(100) substrates heated up to only 200°C. By depositing this type of films on polyimide substrates, we obtain bimorph micro-actuators exhibiting a two-way shape memory effect. A dynamic characterization of these actuators is reported.

SYMPOSIUM H

H-X.5 9:50-10:10

MICROSENSORS BASED ON SEMICONDUCTOR WHISKERS, R. Baitsar, S. Varshava, I. Ostrovskii, State university "Lvivska Polytechnika", 1 Kotlyarevskii str., 290013 Lviv-13, Ukraine

The methods of growing by chemical transport in closed system of Si, Si-Ge, Te-Se, A_3B_5 semiconductor materials in the form of whiskers are considered. The methods allow to obtain in one reactor more than 500 perfect whiskers with necessary parameters and geometry. The whisker size ranges from 0.1 to 100 μm . This is provided by both the selection of technology regime and the doping including complex doping. On the base of the grown whiskers the miniature temperature, pressure, moisture, flow velocity, linea displacement, electromagnetic fields sensors have been developed. Their advantages at the sensors are high sensitivity and stability, low consumer power, wide operation range, etc. For example, the time constant of thermoresistor based on GaAs whiskers consists of a few mc. The physical, technological and design principles of the new type sensors have been offered. Untraditional use of contact phenomena, thermoeexchange and thermoelectrical effects is proposed. New direction in sensor electronics - an elaboration of resonance sensors with frequency output based on the principles of direct transformation of transverse mechanical oscillation of tensosensitive whisker into electrical signal is proposed. The sensors have been tested both in laboratory and industrial conditions in the systems of physical parameter measurement and of the control of ambient pollution.

10:10-10:50

BREAK

SESSION XI - Porous Silicon II

H-XI.1 10:50-11:30 -Invited-

PERMEATED POROUS SILICON FOR HYDROCARBON SENSOR FABRICATION, R. Angelucci, A. Poggi, L. Dori, G.C. Cardinali, A. Tagliani, CNR LAMEL - Institute, via Gobetti 101, 40129 Bologna, Italy

To realise advanced microsensors for a reliable monitoring of very low concentrations of pollutant species such as NO_x , SO_2 , CO, O_3 and aromatic hydrocarbons, the use of porous silicon (PS) layers permeated with mixed semiconducting oxides (Sn-V-O) has been explored. A low concentrations C_6H_6 sensor made of a permeated macroporous silicon layer on a massive Si substrate has exhibited an excellent performance. To reduce the power consumption down to the level reported for micromachined gas sensor (0.1 W), and to make feasible the device to operate in a fast pulsed temperature mode, a novel sensor architecture has been designed. The main feature of the device is represented by a permeated suspended macroporous Si membrane (few tens of microns thick) on top of which a heater resistor and a temperature sensor are integrated. In this paper the PS formation and processing are presented. Results on the morphological and chemical characterization of permeated PS layer are also illustrated. In the end the film conductance changes as effect of the device exposure to gas mixtures of different compositions are shown.

H-XI.2 11:30-11:50

POROUS SILICON FOR OPTICAL WAVEGUIDES: BIREFRINGENCE AND DEPOLARIZATION EFFECTS, M. Le Doucen, J. Charrier, L. Haji and P. Joubert, Groupe de Microélectronique et Visualisation, I.U.T. de Lannion, BP150, 22302 Lannion Cedex, France

In this paper, we study the birefringence and depolarization effects in porous silicon in order to minimize diffusion losses and coupling between optical modes in waveguide structures for telecommunications. Variations of the refractive index in porous silicon multilayers are obtained by changing the porosity and the oxidation degree. The porosity depends on the electrochemical anodization parameters and the substrate doping. This last parameter modifies pore morphology which induces anisotropy of the dielectric tensor and presents the disadvantage to couple modes in optical waveguides.

To date, the birefringence in porous silicon has not been extensively investigated. In this paper, the effects of doping, porosity, and oxidation degree on birefringence values are studied by using propagation of optical modes and polarimetric measurements. In addition, interface rugosity between two layers, which induces diffusion losses in optical waveguides, is deduced from depolarization measurements.

11:50

LUNCH

END OF SYMPOSIUM H

SYMPOSIUM H

SYMPOSIUM H
POSTER SESSION

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

Poster Session

14:00-16:00

- H-P1** MICROSTRUCTURE OF CARBON-COPPER INTERFACE IN COPPER-BASED METAL MATRIX COMPOSITES, A. Berner, Dept. of Mater. Eng., Technion, 32000 Haifa, Israel; K. Mundim and D.E. Ellis, Dept. of Phys. and Astronomy, Northwestern Uni., Evanston, IL 60208, USA; S. Dorfman, Dept. of Phys., Technion, 32000 Haifa, Israel; D. Fuks and R. Evenhaim, Mater. Eng. Dept., POB 653, BGU, Beer Sheva, Israel
Appearance of intermetallic phases at the matrix-fiber (matrix-particle) interface decreases significantly the mechanical properties of the material. The ideal case would be to have a system where the matrix and fiber are mutually nonreactive, insoluble and only wetting occurs between them with modest diffusion bonding. In the most practical systems this is not true, and interaction leads to the formation of the interface region and provides the integration stability of the complex composite. We made the model interface for Cu-C system and carried out high-resolution SEM studies on these samples. It is shown that after heat treatment a narrow interface may be obtained. We also performed microstructural X-Ray investigations of this region and received tendencies to the formation of the nanostructural phase on the interface. Formation of the nano-phase was supported by the MD simulations with potentials derived in the semiempirical approach.
[S. Dorfman and D. Fuks, Composite Interfaces 3, 431 (1996)].
- H-P2** MICROALLOYING OF TUNGSTEN AND INTERATOMIC INTERACTIONS WITH ALLOYING ELEMENTS, D. Fuks and V. Liubich, Mater. Eng. Dept., POB 653, BGU, Beer Sheva, Israel; S. Dorfman, Dept. of Phys., Technion, 32000 Haifa, Israel
The intergranular embrittlement in metals is usually caused by impurities segregating towards the grain boundaries (GBs). The electronic and atomic structure of the tungsten GB and that with the metalloid and metal atoms as dopants is calculated. Perfect and relaxed $\Sigma 3 < 111 > \text{GB}$ is simulated in order to find the most energetically favourable positions of the impurity atom in the GB, and to study the chemical nature of the cohesion, including effects of the electron density redistribution between tungsten and the impurity. Our investigation is a continuation to the recent theoretical analysis, resulted in the predictions of the favourable impurity for ductilizing tungsten by microalloying. These predictions were made on the basis of the "site competition" effect according to which B displaces the harmful impurities off the GBs.
- H-P3** NEW METALLURGICAL SYSTEMS FOR ELECTRONIC SOLDERING APPLICATIONS, C. Gonçalves, J. Ferreira, L. Grigore, I. Ferreira, E. Fortunato, R. Martins, T. Harder*, DCM/FCT-UNL, CEMOP-UNINOVA and CEM, Quinta da Torre, 2825 Monte de Caparica, Portugal; *Fraunhofer Institute, Itzoe, Germany
The aim of this paper is to present results of a new soldering process based on the low-temperature solidification of intermetallic phases which form heat-resistant die-attach as well as signal and power electric contacts. The process leads to the formation of a small gap intermetallic bonding layer in a metallurgical system consisting of a high melting metal (Cu) contact metallization and a low melting metal (Sn) introduced as thin film or preform foil. Because of the total transformation into intermetallic phase, the working temperature of the bond formed is several hundred degrees Celsius higher than the process temperature. Thus, in the system Cu/Sn the process temperature is about 250°C (at a pressure of 2 MPa), the melting temperature of the formed Cu_2Sn intermetallic phase is 640°C. The high melting temperatures of the intermetallic phases (also highly electric conductive) lead to a low homologous working temperature T/T_m of the bond. This is a measure of the velocity of diffusion processes which are the main causes of contact degradation during its lifetime. The process using Cu/Sn system is leading to a homologous temperature T/T_m of about 0.3 compared to 0.7 in the case of soft soldering with SnAg solder alloy. Therefore a better reliability of the proposed bonding process is achievable. Results concerning the match of the predict volume fraction of the intermetallic forms and the experimental measured contact volume will be given, for contacts formed in power diodes using the Cu/Sn/Cu metallurgical system.
- H-P4** ALUMINIUMOXIDE SUBSTRATES FOR THE POWER MICROWAVE AMPLIFIERS, V.V. Murav'ev*, A.A. Tamelo*, U.M. Byahun*, A.M. Nikitin**, U.M. Parkun*, *Belarusian State University of Informatics and Radioelectronics, vul. Petrusya Brouki 6, 220027 Minsk, Belarus; **Minsk Research Institute of Radio Materials, vul. Kizhevataga 86, 220115 Minsk, Belarus
In this paper we will describe the applying of the new technology at creation of the power amplifiers. Using high heat conduction aluminium base of substrate is very important at power circuits. Output power of the microwave amplifier is 1 W at $f=1.7\text{--}2.0$ GHz. Gain is 40 dB at compression of pre-amplification 1 dB.
Aluminiumoxide technology brings the achievement of thin layer dielectric (150 i m), that is the reason of decrease of radiation of the parasitic modes, decrease of jagged AFC at connection of the power amplifiers with previous monolithic cascades.
In general, aluminiumoxide technology is characterised by minimum basic technological operations and materials being used (only Al). It needs common equipment for producing all the important components (substrate, interconnection system, package). It allows effectively to use superficial wiring technique, to produce high-integrated microelectronic assemblies in a frequency range between super-lower and super-high frequencies and at improved thermal, mechanical and radiation characteristics and increased ecological purity.

- H-P5** STRUCTURE AND PROPERTIES OF POROUS SILICON OBTAINED BY PHOTOANODIZATION, E.V. Astrova, V.V. Ratnikov, R.F. Vitman, A.A. Lebedev, A.D. Remenyuk, A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 26 Polytekhnicheskaya, 194021 St-Petersburg, Russia
The results of an investigation of layers of porous silicon (PS), which was obtained by electrochemical etching of p-Si under different illumination conditions - natural light, incandescent light, and light from a mercury lamp with and without a filter - are reported. The structure of the layers was studied by double-crystal x-ray diffractometry, the composition was monitored by means of the IR absorption spectra, and the radiative properties were monitored according to the photoluminescence (PL) spectra. It was established that electrochemical etching under illumination produces PS with a higher porosity and more intense PL whose maximum is shifted into the short-wavelength region. These changes are accompanied by a large disordering of the structure and an increase in the oxygen content in the layer. It is concluded that illumination accelerates the chemical interaction of PS with the electrolyte due to oxidation. High-porosity porous silicon stored in air exhibits quenching of PL. Conversely, PL is excited in layers with a lower porosity. Aging of PS is characterized by an increase in the microdeformation of the layers, a decrease in the crystallite sizes with a partial loss of coherence between the crystallites and the substrate, and an increase in the fraction of the amorphous phase.
- H-P6** OBTENTION AND CHARACTERIZATION OF BIO-ENGINEERED LAYERS ONTO SILICA BASED MICRO-STRUCTURES, S. Falipou, J.-M. Chovelon, C. Martelet, Laboratoire d'Ingénierie et Fonctionnalisation des Surfaces, CNRS/UMR 5621, Ecole Centrale de Lyon, BP163, 69131 Ecully Cedex, France and J. Margonari, D. Cathignol, INSERM, Unité 281: Recherches sur la Détection et le Traitement de la Prolifération Tissulaire par Agents Physiques, 151 Cours Albert Thomas, 69424 Lyon Cedex 03, France
In this communication, we present a simple protocol to fix biological species to silica based surface: glass slides and silica beads. A monofunctional silane reagent 3-cyanopropyltrimethylchlorosilane was used to modify the surface of silicon wafers and appeared to be able to strongly attach soluble antibodies through their glycosylated regions (OH groups) to solid supports. Such silane reagent was used without further derivatization. Antibodies anchored, in a following simple incubation step, were proved to be able to fix CD45 rat cells on floating silica hollow microbeads. The originality of this study is that this type of hollow, low-density silica microbeads have never been used before. Moreover, it could be used in ultrasounds applications, thus a further destruction of cells selectively fixed on such support could occur, using cavitation phenomena. Such a study can serve as a model of micro-biosystem involving cells manipulation.
- H-P7** CHARACTERIZATION OF THE NONLINEAR OPTICAL PROPERTIES OF CRYSTALS BY THE SHEW TECHNIQUE, R. Kremer, A. Boudrioua and J.C. Loulergue, Laboratoire MOPS / CLOES, 2 rue E. Belin, 57070 Metz, France
These past few years, the development of new compact and coherent laser sources using second harmonic generation (SHG) has been subject to many research works.
The design of devices based on SHG requires to characterize the nonlinearity of the material (id. the nonlinear coefficients). For this reason, Kiguchi & al. proposed some years ago the Second Harmonic wave generated with Evanescent Wave (SHEW) method. The latter was mainly used to investigate organic compounds in powder form.
This technique takes advantage of using an evanescent wave under total reflection conditions to induce a SH wave in the nonlinear medium. Therefore, it is very suitable for evaluating nonlinearity of layered materials.
For our study, we used the SHEW method to estimate the nonlinear coefficients of LiNbO_3 both in bulk crystals and in waveguide structures elaborated by implantation of light ions (H^+ and He^+).
For various polarization and different cuts of the crystal, the SH power recorded versus the incidence angle gives the components of the nonlinear tensor. The results point out that the nonlinear optical properties of the crystal are preserved after implantation. Other crystals such as BBO and LiTaO_3 are also under investigations.
- H-P8** MECHANICAL STABILITY OF RF-SPUTTERED AND RTA-ANNEALED $\text{Pb}(\text{Zr,Ti})\text{O}_3$ THIN FILMS, E. Defaÿ, M. Leberre, B. Semmache and D. Barbier, Laboratoire de Physique de la Matière, Bât 502, INSA de Lyon, 20 av. A. Einstein, 69621 Villeurbanne Cedex, France
PZT thin films were prepared on a $\text{Si}/\text{SiO}_2/\text{Ti}/\text{Pt}$ substrate by RF-magnetron sputtering using a stoichiometric $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ target.
An investigation method, based on an orthogonal array, showed a clear dependency of the PZT thin films mechanical stability on the sputtering pressure after the crystallisation Rapid Thermal Annealing (RTA) at 600°C during 30s in air.
This phenomenon was correlated with an in-depth Pb-gradient in the PZT film, as observed on cleaved surfaces by Energy Dispersive Spectroscopy (EDS) and Secondary Ion Mass Spectrometry (SIMS). This showed that the in-depth Pb-gradient can be drastically reduced when the sputtering pressure was increased from 2.10^{-2} mbar to 8.10^{-2} mbar. Hence, the higher the sputtering pressure, the lower the Pb-gradient and the better the mechanical stability of the PZT films. However, high sputtering pressure did not lead to the highest deposition rate.
Furthermore, the PZT mechanical stability was further enhanced by preannealing of the Pt/Ti bottom electrode (RTA : 400°C 30s in Argon), allowing in addition the desired (111)-orientation of the PZT perovskite phase, as observed by X-Ray Diffractometry (XRD).
- H-P9** GROWTH OF $\text{Li}_x\text{Mn}_2\text{O}_4$ AND LiCoO_2 THIN FILMS ELECTRODES FOR ELECTROCHEMICAL SENSORS, M. Morcrette, A. Laurent, P. Barboux*, T. Brousse**, J. Perrière; Groupe de Physique des Solides, Universités Paris VII et Paris VI, Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France; *Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cedex, France, **Laboratoire de génie des Matériaux, ISITEM, Rue Christian Pauc, BP 90604, 44306 Nantes Cedex 3, France
 LiMn_2O_4 is a suitable material as a positive electrode in secondary Li ion cells. In this work, we have studied the growth of thin films of this compound by laser ablation of a LiMn_2O_4 target. Films have been deposited onto Si (100) and platinum substrates at different T (300 to 700°C) under O_2 pressure (10^{-6} to 1 mbar). Under high T and low oxygen pressure a lack of the Li is evidenced by Nuclear Reaction Analysis. X-Ray diffraction analysis evidenced the formation of the spinel phase for films grown under high O_2 pressure.
The cyclability of our films has been checked in classical Li-ion battery at a high scan rate giving a low loss of capacity (<25%) after 450 cycles. The films have been also used as a selective electrode for Li ions. The electrochemical potential of our films versus ECS is a linear increasing function of the Li concentration from 10^{-4} mol.l $^{-1}$ to 10^{-1} mol.l $^{-1}$ with a very fast response (<2s). These films present a high selectivity versus Na^+ and K^+ . Then, these films could be used as a selective Li electrode and are of interest in analytical measurement in medicine.
 LiCoO_2 has also been studied for its good electrochemical properties. Crystalline quality and good composition are also obtained at high O_2 pressure and low T (500°C). Selectivity have also been measured versus Li in solution.
- H-P10** SCANNING ACOUSTIC MICROSCOPY: A TOOL FOR MEASURING CROSSLINKING GRADIENTS IN PHOTOPOLYMER MATERIALS, L. Simonin, J.J. Hunsinger and D.J. Lougnot, Equipe Microscopie acoustique, LERMPS, Institut Polytechnique de Sévenans, 90010 Belfort Cedex, France
Acoustic microscopy, widely used in the non destructive testing of various materials (ceramics, metals, biological media, polymers,...), makes it possible to study micromechanical properties and to locate defects or discontinuities at the surface of optically opaque materials.
The crosslinking gradients in a photopolymer material with a curved surface can be determined using acoustic techniques. The reflection coefficient at the liquid/material interface measured by low frequency microechography is related to the mechanical properties of the material and also to the profile of the surface. A new procedure is presented: this method makes it possible to remove the effect of relief and local slope and to obtain a real map of mechanical properties, in particular of crosslinking density changes in polymer materials.

- H-P11** PREPARATION OF THIN FILMS OF COPPER(I) BROMIDE FOR GAS SENSORS, J-L. Seguin, M. Bendahan, P. Lauque, C. Jacolin, M. Pasquinelli* and P. Knauth**; Laboratoire d'Electronique et Physicochimie des Couches Minces, Case A62; *Laboratoire Défauts dans les Semiconducteurs et leurs Oxydes, Case 231; **Laboratoire EDIFIS-Metallurgie (AMR CNRS 6518), Case 511, Faculté des Sciences de Saint Jérôme, 13397 Marseille Cedex 20, France
Solid ionic conductors have many applications in the field of electrochemical sensors. Copper halides are Cu^+ ion conductors with an interesting possible valence change of copper (Cu^{2+}).
The aim of our study is :
i) to prepare thin films of copper(I) bromide,
ii) to study the feasibility of electrochemical gas sensors using this material.
We describe the preparation of copper(I) bromide films on various substrates by r.f sputtering. The influence of the sputtering parameters on the film structure and composition is studied. Polycrystalline films with the $\gamma\text{-CuBr}$ structure and randomly oriented grains in the micrometer range are obtained. The electrical behaviour of the material is characterised using current-voltage measurements which suggest a p type conductivity of CuBr films.
- H-P12** NiTi THIN FILMS AS A GATE OF MOS CAPACITY SENSORS, K. Aguir, M. Bendahan, J-L. Seguin and H. Carchano, Laboratoire d'Electronique et Physicochimie des Couches Minces, Case A62, Faculté des Sciences de Saint Jérôme, 13397 Marseille Cedex 20, France
In this study, a NiTi-shape memory alloy thin film is used as a gate in a MOS-type structure.
The shape memory effect involves a thermally induced phase transformation between a low temperature ductile phase and a high temperature high strength phase.
The NiTi gate is deposited on SiO_2/Si substrate using RF sputtering deposition method.
We have studied the evolution of C(V) characteristics in function of temperature in order to provide evidence of phase transition within the NiTi layer, and also to investigate the effect of such a transition on the electrical properties of the structure.
A rapid change in the C(V,T) curves which is a direct consequence of the modification in the NiTi structure is observed and discussed.
The possibility of realizing a sensor of current to be integrated in microelectronic process and power integrated circuits is envisaged.
- H-P13** MECHANISM OF POROUS SILICON FORMATION BY SPECIFIC SURFACE CHEMISTRIES, V. Polishchuk, E. Souteyrand, J.R. Martin, V. Skryshevsky, V. Strikha, IFoS-Groupe PCI, Ecole Centrale de Lyon, 36 Av. Guy de Collongue, BP163, 69131 Ecully Cedex, France
The anodic current-potential characteristics of p-doped silicon substrates with $\rho=4.5 \Omega \text{ cm}$ in different solutions are studied. From the analysis of these characteristics the thin oxide layer growth is shown at the silicon-electrolyte interface during anodisation processes. The chemical reactions of anodic silicon oxidation are discussed. The forming of Si-OH , Si-H and SiF_2 species on silicon electrode thanks to the electrochemical reactions of silicon with HF and H_2O in $\text{HF}/\text{H}_2\text{O}$ /Ethanol electrolyte leads to a kinetic competition between surface oxide formation and its dissolution by HF. The model of porous silicon formation is suggested and the current - electrolyte composition dependence is given by Nernst equation. The band gaps of films - were defined from optical absorption spectra for different electrolyte compositions. For porous silicon films etched at the same anodisation conditions ($J=15 \text{ mA/cm}^2$, $t=3 \text{ min}$) the value of band gap in range from 2.5 till 2.8 eV is function of $x=[\text{H}_2\text{O}]/[\text{HF}]$, where $[\text{HF}]=24\%$ and $x=1.08\text{-}2.87$. The band gap decreasing with x is explained by oxide layer growth that confirms the proposed model of porous silicon formation.
- H-P14** A THERMOELECTRIC CONVERTER FOR ENERGY SUPPLY, H. Glosch, M. Ashauer, U. Pfeiffer*, W. Lang, HSG-IMIT: Hahn-Schickard-Gesellschaft, Institute of Micromachining and Information Technology, Wilhelm-Schickard-Str. 10, 78052 Villingen-Schwenningen, Germany; *KUNDO Systemtechnik, St. Georgen, Germany
A thermoelectric power generator in silicon technology is used for the energy supply of low power systems. An electrical power of $1.5 \mu\text{W}$ is generated with a temperature difference of 10°C .
An important application of MEMS are small, independent and wireless systems for remote sensing, control, safety surveillance and metering. Energy supply is mostly done with a battery with all the severe drawbacks mainly its disposal because of the chemistry which is harmful to the environment. As a widespread solution the solar cell is used for small calculators or watches. If there is no light yet another possibility is interesting: small temperature differences which are present almost everywhere can be used by a thermoelectric converter. Therefore small, inexpensive and efficient converters will have important applications to replace batteries in many systems. This paper describes the development, technology and characterisation of a silicon thermoelectric energy converter. In order to achieve a reasonable voltage the manufactured prototype uses a number of 1000 thermocouples generating a total voltage of 2.2V at a temperature difference of 25°C . The electrical power is sufficient to operate a small preamplifier and sensor control system. For complexer applications a generator with a power in the region of $20 \mu\text{W}$ would be desirable. Therefore at the moment, a second generation of the device is planned which will reach 10 times the efficiency.
- H-P15** GALVANIC POROUS SILICON FORMATION WITHOUT EXTERNAL CONTACTS, C.M.A. Ashruf, P.J. French, Delft University of Technology, PO Box 5031, 2600 GA Delft, P.M.M.C. Bressers, ECN, PO Box 1, 1755 ZG Petten, J.J. Kelly, Utrecht University, PO Box 80000, 3508 TA Utrecht, The Netherlands
Formation of porous silicon is usually accomplished by electrochemical etching in an HF solution. The holes, required for the dissolution of silicon and pore formation, are supplied by a power supply. Although this method works well, the requirement for external contacts is not convenient. A porous formation technique which does not require external contacts is 'stain etching', using an HF/HNO_3 solution. The disadvantage of this electroless etching technique is that the reduction reaction required for hole injection is autocatalytic. As a result porous formation is preceded by an incubation time leading to poor control and reproducibility. Here we present a different approach for forming porous silicon under open-circuit conditions. By connecting a silicon sample to an inert electrode a galvanic cell is formed. The inert electrode has also been formed by evaporation of a gold/chromium layer on the silicon wafer. Holes, required for the pore formation, are now supplied by the reduction of oxygen in the HF solution at the inert electrode. Both in p-type Si and n-type Si (under illumination) porous layers have been formed without external bias. Porous layers formed in approximately 5 minutes, with a thickness of $300 \text{ nm} \sim 1.6 \mu\text{m}$ (depending on process parameters), have shown clear photoluminescence. In conclusion, porous silicon has been formed under open-circuit conditions with a good reproducibility.
- H-P16** THE MOST POSSIBLE DISTORTIONS TYPICAL FOR LAYER CRYSTALS WITH $\text{P6}_3/\text{mmc}$ STRUCTURE, O.A. Buryi., C.C. Tovstjuk, Semiconductors department, State University "Lvivska Polytechnica", Bandera street, 12, 290646, Lviv, Ukraine
The pseudo Jahn-Teller effect for layer crystals ($\text{P6}_3/\text{mmc}$ space group) is considered. The adiabatic potential calculation is carried out numerically and agrees with analytical calculations for asymptotical cases: (i) some vibronic constants are equal; (ii) some of them are neglected. We obtained four different adiabatic potential surfaces, which can provide the specific polarization properties of the crystal. We calculate different thermodynamical functions for every obtained adiabatic potential type. Our results are in good agreement with the same ones known before. These investigations allow to choose adiabatic potential type advantageous from the thermodynamical consideration. It is shown the two valleys adiabatic potential surface is the most advantageous, that's why it will occur in most cases. The second probable surface consists of two equivalent and one shallow valleys. These adiabatic potential types allow to determine the possible ions distortions from the equilibrium states because of the electron gas influence. The thermodynamical potential (as well as entropy) calculations show that these distortions are more probable than the non-distorted state in such crystals.

- H-P17** DENSITY DETERMINATION OF MATERIALS IN MICROSTRUCTURES BY RBS METHOD, V.K. Egorov, I.A. Sosnin, Lab. Nucl. Phys. IPMT RAS, Chernogolovka, Institute prospect 19, 142432 Moscow dist., Russia; O.S. Kondratiev, Mech. and Math. Dept., Moscow State Univ., Moscow, Russia
Density of materials in the fine flat structures is recognized as constant usually in spite of the experimental data show clear evidence of being varied [1]. The procedure of the direct materials density determination in target layers derived from RBS data for the target is suggested. There is discussing the model of metal fcc structure enabled to co-ordinate the outline amplitude of RBS He⁺ ion spectra from the tested specimen with material's density derivation from its "X-Ray value" [2]. The model is founded on idea of the regularity conservation in volume electron density at random distribution of vacancy in the crystalline structure. Within the model a possibility of the quantity material's density determination on based of RBS data only is justified. The experimental data of RBS He⁺ (E₀=1.5 MeV) on Al and Ag films allowed the determination of the real materials density directly are discussed. There are described the conditions needed for the density testing measurements connected with an ion scattering. The factors influenced on the accuracy of such measurements are analyzed.
[1] V.K. Egorov, O.V. Kononenko, O.S. Kondratiev, Poverkhnost (Fiz. Khim. Mekh.), # 6, 1997, p.p.73-85, in Russian.
[2] B.D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley P.C.I., London, 1978, p. 88.
- H-P18** ELECTROPHYSICAL PROPERTIES, MICROSTRUCTURAL FEATURES AND SYNTHESIS OF SOLID SOLUTIONS BASED ON BARIUM TITANATE, Y.I. Luzhetskyy, Non-Linear Sensors Laboratory, Drohobych State Pedagogical Institute, 24 Iv.Franko Str., 293720 Drohobych, Lviv Region, Ukraine
Solid solutions based on barium titanate are widely used for positive temperature coefficient (PTC) thermistors creation. Ceramics (Ba_{1-x}Ca_x)(Ti_{1-0.025-0.1}Nb_{0.025-0.1}Mn_{0.025-0.1})O₃ was synthesized with the aim to establish the interconnection between the microstructure, doping processes and electrical properties of ceramics. Structure of investigated materials was studied by electron microscopy (Jamp-10S) and X-ray phase analysis (HZG-4a) methods. Electrical properties were investigated in wide region of temperatures and electric field strengths. Structural investigations showed that Nb, Mn and Ca dopes influence considerably on grain dimensions and electrical conductivity of ceramics. Isovalency replacement of Ba by Ca (x≤0.1) leads to the decreasing of average grain dimensions and the appearance of microregions with different phase compositions. Doping of BaTiO₃ (j=0.003) by Mn (k=0.0011) changes only the value of conductivity but at k=0.0007 and 0.004≤j≤0.006 the grains growth was renewed. It was established that the value of varistor effect depends strongly on average grain dimensions.
- H-P19** THE PHONON PARTICULARITY OF INSE, BAND EN THE ELASTIC PROPERTIE, O.V. Stachiv, C.C. Tovstyuk, Semi-conductors Department., State University "Lviv Politechnica", Bandera str. 12, UA 290646, Lviv, Ukraine455
The InSe phonon spectrum was calculated in continual approximation, using the experimental data of elastic constants temperature dependence. Two ellipsoidal isoennergetic surfaces (IES) -for one quasilongitudinal and transverse dispersions and one very special, pillow-like surface for quasitransverse dispersion. We analysed IES for different crystals and obtained that pillow-like surfaces are typical only to layer crystals (LC). The IES are functions of the quasiimpulse and the temperature. These three IES have sufficiently different dependences on the temperature. As a result, in InSe with temperature increasing up to 400K we observe the pillow-like surface transformation to the ellipsoidal one. Temperature increasing destroys the particular form of IES in LC. Phase velocity, and, as a result, Debye temperature (DT) become over by the temperature increasing. It is shown that the DT dependence can be approximated by: DT=231.5-0.16*T. We calculated the temperature dependences of such thermodynamical values as: entropy, enthalpy and heat capacity. For the acoustical phonon gas in InSe they are different from the classical ones.
- H-P20** IR OPTICAL PROPERTIES OF ORGANIC DYE LAYERS PRODUCED AT DIFFERENT TECHNOLOGICAL REGIMES, L.V. Poperenko, K.L. Vinnichenko, Taras Shevchenko Univ., 252022 Kyiv, Ukraine, V.G. Kravets, Inst.for Inform. Rec.Probl., Kyiv 252113, Ukraine, A. Roeseler, ISAS-LSMU, 12489 Berlin, Germany
The IR optical properties of the organic materials being used as an optical information recording media were investigated. Three types of the pyrozo-lin-based dyes were considered. They were classified by the absorption band position in the visible spectral region as a bright-red, bright-orange and orange-red dyes. The films of these dyes were deposited at the glass and silicon substrates at the different technological regimes. It is defined that optical constants of all dyes significantly depend on such technological conditions of the films deposition as the distance from the sample to evaporator in vacuum chamber, vapor pressure, material of the substrate, but the absorption band at the frequencies 1200-1500 cm⁻¹ is typical for all coatings investigated. It is revealed that spectra of the ellipsometric parameters Δ as well as Ψ for such reflecting systems as Cr film on glassy substrate and bright-orange dye layer deposited on such a system coincides in the frequency range 500-1000 cm⁻¹. The data obtained would allow to optimize organic dye film's deposition technology for optical recording.
- H-P21** REM-STUDY OF ELECTROCHEMICAL FORMED PILLARED MICROSTRUCTURES, A.I. Vorobyova, E.A. Outkina, Belorussian State University of Informatics and Radioelectronics, 220027 Minsk, P.Brovky str. 6, Belarus
The REM-study of the electrochemical formed pillared microstructures are performed. The pillared microstructures were formed by means of multi-step electrochemical anodization of Ta/Al thin film composition on ceramic and silicon substrates. Microstructure and composition of the combined anodic oxide film (AOF) and pillar microstructures were investigated with JEM-S-80 scanning electron microscope and JSM-35 electron microscope. The information on geometrical parameters of porous host and pillar microstructure elements are determined by composition of the anodization electrolyte and conditions. The depth:diameter ratio ("aspect ratio") for investigated composition was 1,7-10, the pillars density ñ (3 (109 (2,6(1010 cm ñ 2, pillars radius ñ (15(80) nm.
- H-P22** THE InTiH SEMICONDUCTING SUBSTITUTIVE SOLID SOLUTION INCORPORATED INTO ZEOLITE MATRIX, R. Peleshchysyn, A. Frani, Experimental Physics Dept. of Lviv State University, 50 Dragomanova St., 290005 Lviv, Ukraine and M. Bublyk, Lviv Institute of Management, 57, 700-richchya mista Lvova St., 290601 Lviv, Ukraine
The paper deals with the problems of creating new materials on the base substitutive solid solutions of the semiconductor crystals incorporated into zeolite matrix. In_xTi_{1-x}I (0.2≤x≤0.95) semiconducting substitutive solid solutions and Na₈[Al₈Si₄₀O₉₆]•24H₂O natural zeolite of the mordenite type (Na-MOR) in the matrix role have been used. The method of preparing the In_xTi_{1-x}I clusters based on the thermovacuum processing. The natural mordenite has the one-dimensional emptiness with the diameter of 6.7x7.0 Å. The In_xTi_{1-x}I unit cell parameters are within a=4.6÷4.7 Å, c=4.9÷5.1 Å, b=12.8 Å. Na-MOR samples were powdered and dehydrated in vacuum. It is determined that Na-MOR gives back the all water at the 823 K during 3-6 hours without crushing of the space structure of the zeolite framework. In_xTi_{1-x}I molecules were incorporated into the zeolite supercages by physical absorption. Optimal temperature regime are within 653÷713 K respectively to In/Ti ratio. The zeolite samples were cooled to room temperature gradually. The uninterrupted set of the substitutive solid solutions In_xTi_{1-x}I use as a model objects with the determined optical properties. Therefore, investigation of In_xTi_{1-x}I clusters and molecules has scientific and applied important.

- H-P23** SOME PARTICULAR ASPECTS OF DEFINE THE THICKNESS OF THE MEMBRANE BY BORON DIFFUSION PROCESSES, E. Manea, R. Muller, A. Popescu, National Institute for Research and Development of Microtechnology PO box 38-160, Bucharest, Romania
Micromachining techniques have an increasing importance in the development of microsensors applications. For free standing 3D structures bulk and surface micromachining are used.
These paper presents experimental results concerning thin membranes, realized by p⁺ etch stop techniques. We obtained a concentration of $1 \times 10^{20} \text{cm}^{-3}$ through thermal diffusion from Boron⁺ solid source by a performed program (thermic cycles). This value is enough for stop-etch layer in anisotropic etching of silicon (100) in KOH solution at 80°C. Spreading resistance has measured the Boron profile.
The wafers were processed in two ways. Some of them were boron diffused over the entire area of the wafer and other were diffused only in pattern geometries, define in silicon after thermal oxidation. In this case we have used double side alignments.
We define square geometries for membranes, with 1.5 and 2.5 mm² areas.
The performance result could be noticed from the thickness of the membranes of 10-12µm with good uniformity on wafers.
- H-P24** OPTICAL SYSTEM AND METHOD FOR REAL TIME POSITION CONTROL IN EXPERIMENTAL EQUIPMENT FOR LOCAL IRRADIATION, R. Rădvan, D. Ghica, R. Savastru, National Institute of Optoelectronics, PO Box MG-22, 76900 Bucharest, Romania
The paper presents an original improvement of an optical equipment for experimental studies and special patterns generation. The system is an specialized microscope with classical optical devices for visualization, and image recording, improved with some special light sources.
The modifications of the photosensitive layer after irradiation and before chemical processing of the sample are not visible and the right position can be easily lost.
The proposed optical system used two different reticules with special configuration. One of these reticules is used like an vernier and the second like a cursor.
A simple optical arrangement on the same microscope can be used for the thin layer quality investigation.
- H-P25** POROUS SILICON CONTROL IN SITU AND THE AMBIENT INFLUENCE ON ITS PROPERTIES, D.I. Bilenko, O.Ya. Belobrovaja, O.Yu. Coldobanova, E.A. Jarkova, E.I. Khasina, V.P. Polyanskaja, T.E. Mel'nikova, I.B. Mysenko, V.V. Smirnov, Saratov State University, Russia
Porous silicon (PS) is a perspective material for the Microsystems because of (i) its unique possibility of the local transformation of Si into a set of new materials with unusual functional properties and (ii) compatibility with VLSI technology.
In situ control of the process of formation of low- dimensional PS structures was developed. It allows to determine the layers thicknesses and porosity which directly connected with technological, physical and functional, particularly, sensorical, properties. The method is based on the measurements and analysis of polygarmonic time dependence of the radiation, reflected from the forming structure.
The high sensitivity to H₂S was found in structures with PS layers, with catalytic (Pd, Ni) and ohmic (Al) electrodes. In the best samples the appearance of 3 molecules H₂S on 10⁹ molecules N₂ increased the electrical current value in 2-3 times. The structures are able to measure selectively H₂S concentration from 0.02 to 100 ppm. In such structures the sign and magnitude of built-in open circuit potential is controlled by ambient gases, potential base and optical excitation.
It is found an unusually high reversible and nonreversible optical properties changes because of the gas solvents and alcohol influence. For example, the exposure of PS layers in ethylalcohol vapor changes a color of PS from brightly blue to crimson and the refraction coefficient in IR region changes up to 0.06.
- H-P26** MICROSYSTEM STRUCTURES CONTROL IN SITU, D.I. Bilenko, O.Ya. Belobrovaya, O.Yu. Coldobanova, A.I. Smirnov, V.V. Smirnov, V.D. Tsiporukha, Saratov State University, Russia
The possibilities of precision multiparametric control of structures directly in the course of basic MEMS formation processes (epitaxy, plasma deposition and etching, vacuum evaporation, electrochemical and chemical processing and composition modification) are reported. Main objects of control *in situ* include multilayer structures and structures with developed volume topology on the base of: crystalline, amorphous, polycrystalline and porous Si, oxide and nitride Si, semiconductors of A₂B₆ group, GaAs, Ga_{1-x}Al_xAs, including quantum-dimensional structures and composite materials.
The created methods are based on interference, diffraction and polarisation of radiation reflected from the forming structures, which dimensions may be essentially smaller than a minimal radiation wave length.
It was found that optical properties of complex semiconductor materials have the sensitivity maximum to the changes of composition and topological sizes in the range of the energy spectrum critical points. On this basis the control of composition and thickness in the course of molecularbeam epitaxy of GaAs/Ga_{1-x}Al_xAs superlattices was experimentally realized with the errors in $x < 0.02$ and $d < 3 \text{ nm}$.
The significant features of created methods and hardware are their availability and reliability. They are effective in the direct process control and creating of the math speculation of the process..
The possibilities of forecasting of the structures functional parameters and technology optimization on the basis of the multiparameters *in situ* control are experimentally confirmed. For example, functional parameters of a-Si:H based photoconvertors have optimum in strictly confined range of measured *in situ* properties (refraction and extinction coefficients, and growth velocity).
- H-P27** POROUS SILICON AS SUBSTRATE FOR IONS SENSORS, M. Ben Ali, R. Mlika and H. Ben Ouada, Laboratoire de Physique des Interfaces, Faculté des Sciences de Monastir, Route de l'Environnement, 5000 Monastir, Tunisia; R. M'ghaieth and H. Maaref, Laboratoire de Physique des Semiconducteurs, Faculté des Sciences de Monastir, Route de l'Environnement, 5000 Monastir, Tunisia
Electrochemical anodisation of lightly doped (100) p-type silicon is used to achieve porous layers with high-porosity (80%) in which the specific surface area is in the range 500-600 m²/cm³. The thickness layer is time anodisation dependent and optimised for this purpose at 2µm to avoid cracking. This layer was thermally oxydised by Rapid Thermal Oxydation (RTO) technique which allows the fonctionnalisation of the large surface area and then used as substrate for ions sensors.
Thin calix[4]arene film was deposited using thermal evaporation under vacuum to fabricate microsensors based on an E.I.S (Electrolyte-Insulator-Semiconductor) structure on two type of substrates: the previous p-Si described and the p-type Si/SiO₂ plane substrate.
A comparative study shows that a surnernstian response (100 mV/decade) was measured in the first case which behavior has been observed with incorporated ionophores in plasticized PVC membrane or in polysiloxane gel. However, in the second case, in which a calix[4]arene layer thermally deposited on the silica membrane of an ISFET and on EIS structure, a nernstian response has been reported. Thus, an analogy between porous silicon and coupling agents (PVC or gels) based membranes can be established.

E-MRS'98 SPRING MEETING



SYMPOSIUM I

Rapid Thermal Processing

Symposium Organizers

A. SLAOUI CNRS/PHASE, Strasbourg, France
J.C. MULLER CNRS/PHASE, Strasbourg, France
T. THEILER STEAG-AST, Dornstadt, Germany
R.K. SINGH University of Florida, USA

The assistance provided by

J.I.PELEC

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is acknowledged with gratitude.

(France)

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SYMPOSIUM I

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - Equipments in RTP

Chairperson: F. Roozboom, Philips Research, Eindhoven, The Netherlands

- I-I.1** 9:00-9:30 - Invited - **RAPID THERMAL PROCESSING TECHNOLOGY FOR THE 21st CENTURY, P.J. Timans**, AG Associates, 4425 Fortran Drive, San Jose, CA 95134-2300, USA
Rapid thermal processing (RTP) provides unique capabilities for the development of advanced semiconductor device manufacturing processes.
New generations of RTP equipment incorporate sophisticated hardware developments, many of which are aimed at providing excellent thermal control, for both 200 and 300 mm wafer sizes. This paper will review recent developments in RTP system design, focusing on the physics underlying the system design, and illustrating how simple thermal models can be used to assess many of the fundamental design problems. The paper will also describe results obtained for several advanced processes using the latest RTP technology.
- I-I.2** 9:30-9:50 **QUARTZ INFRARED HALOGEN LAMPS FOR SEMICONDUCTOR WAFER HEATING, A. Lang and S. Chehu**, Philips Lighting, Chemin de Montrichard, B.P. 149, 54705 Pont-A-Mousson Cedex, France
Heating technology plays an essential role in semiconductor wafer manufacturing, especially in epitaxy and rapid thermal processing (RTP). The most common radiative source used is the quartz infrared halogen lamp. There are nowadays more and more developments going on using these heating lamps. The lamp is usually not the primary focus of the project engineers in the semiconductor world. However, lamps have to be designed and used in the correct way in order to provide the best service to end users.
Thus the aim of this paper is to provide an overview on the key specifications of the halogen lamp. The first part will concern the principles of infrared radiation, the halogen cycle, and the main lamp features. The second part will concern the most important parameters involved for having a good reliable lamp in the reactor: among others, the influence of filament design, voltage supply, reflector shape and cooling will be discussed in detail.
- I-I.3** 9:50-10:10 **SPECIFIC RTP EQUIPMENT FOR DEEP JUNCTION FORMATION, J.M. Dilhac**, L. Cornibert, C. Ganibal, C. Lancelle, LAAS-CNRS, 7 avenue du colonel Roche, 31077 Toulouse CEDEX, France
Power devices often need very deep diffusions extending through the thickness of the wafer to provide junction isolation of the vertical power components. In addition, applications such as circuit breakers for protection require the fabrication of two-direction structures, occupying the whole silicon thickness and emerging on both sides. Highly doped vertical walls are therefore required both for total vertical junction insulation of devices, and alternatively as a permanent conducting link between device surfaces. The generally used method of fabrication for these junctions is based on a high (1300°C) temperature redistribution during several days (300 hours) applied to relatively thin (200 µm) wafers. The obtained junctions are about twice as wide as their depth, leading to a large surface consumption. Moreover, the wafer warpage after redistribution jeopardizes the following process steps, and the induce surface defects are incompatible with the fabrication of MOS gates. In this paper we report our investigations to replace this standard process, with Temperature-Gradient Zone Melting, where a molten silicon/aluminium solution moves through a Si wafer in minutes, leaving a highly Al doped trail behind it. We used a specific Rapid Thermal Processor made up of a single row of tungsten halogen lamps suspended below a reflector, on one side of a quartz processing chamber. A black water-cooled base on the other side acts as a radiative heat sink. The task of this base is critical: it has to absorb the radiations emitted by the non-illuminated surface of the wafer, to create a controlled temperature gradient between the back and front surfaces. The liquid phase diffusion of Al is driven by this vertical thermal gradient. The emergence of the melted alloy is detected optically in situ, and the processor is power controlled.
- I-I.4** 10:10-10:30 **RTP EQUIPMENT DEVELOPMENT FOR SOLAR CELL PRODUCTION, B. Groh, T. Theiler**, STEAG-AST Elektronik GmbH, Daimlerstr. 10, 89160 Dornstadt, Germany
High efficiency and low cost are the keys for photovoltaic systems to become competitive compared to conventional energy sources. It has been shown in the past that RTP is a promising method towards this aim, as good results on solar cell efficiencies have been reported by different laboratories. RTP systems have to be adapted to the demands of solar cell manufacturing, especially the desired high throughput.
Since temperature gradients up to 200 K/s are possible and gases can be exchanged very quickly, RTP allows to realize sequences of different process steps in the same process chamber.
STEAG-AST Elektronik GmbH will present specifications of their available RTP equipment with respect to a solar cell continuous processing line. Calculations of throughput and energy consumption are carried out for all relevant process steps that can be performed by RTP, such as emitter formation or oxidation, and compared to conventional thermal processing.
- 10:30-11:00 **BREAK**

SYMPOSIUM I

SESSION I- Modeling & Control in RTP**Chairperson: R. Singh, Clemson University, Clemson, USA**

- I-I.5** 11:00-11:30 - Invited - **MODELLING AND OFF-LINE OPTIMIZATION OF 300MM RAPID THERMAL PROCESSING SYSTEM, A. Tillmann, STEAG AST Elektronik GmbH, Daimlerstrasse 10, 89160 Dornstadt, Germany**
The modelling of a new 300mm Rapid Thermal Processing (RTP) system is described. Conventional raytracing technique is used to determine lamp intensity distributions on both 200 and 300mm wafers. Simulation results are verified using the "difference method" (difference between two process parameter distributions such as oxide thickness, where the absolute power of one single lamp is varied) and using wafers instrumented with multiple thermocouples.
Wafer rotation is incorporated in the model and its influence on the temperature distribution will be discussed.
Off-Line optimization of the temperature distribution is done using model-based control. Experimental results of implant annealing, Rapid Thermal Oxidation (RTO) and silicidation processes on both 200 and 300mm are shown and critical parameters influencing the temperature uniformity are discussed.
- I-I.6** 11:30-11:50 **PERSPECTIVES ON EMISSIVITY MEASUREMENTS AND MODELING IN SEMICONDUCTORS, N.M. Ravindra, B. Sopori*, S. Abedrabbo and W. Chen*, New Jersey Institute of Technology, Newark NJ 07102, USA; *National Renewable Energy Labs, Golden CO 80401, USA**
An overview of the emissivity measurements and modeling techniques available to the semiconductor industry is presented. This study focuses on methodologies that are being implemented for ex-situ and in-situ process monitoring and control. The role of surface roughness in influencing the radiative properties of silicon is discussed. Comparisons between model based simulations and experimental results are presented. Advantages of the proposed experimental techniques in terms of its ability to deconvolute the measured properties to yield the unknown fundamental optical constants of materials are demonstrated. These studies have been performed for temperatures in the range of room to 1000°C and wavelength range of 1 to 20µm.
- I-I.7** 11:50-12:10 **NEW METHODS OF METROLOGY DATA ANALYSIS DURING SEMICONDUCTOR PROCESSING AND APPLICATION TO RAPID THERMAL PROCESSING, M. Boin, Scientific Software, Graf-Albrecht-Str. 24, 89160 Tomerdingen, Germany; W. Lerch, STEAG AST Elektronik GmbH, Daimlerstr. 10, 89160 Dornstadt, Germany**
Three new mathematical methods to analyse data derived by semiconductor metrology tools are presented in this paper. These methods are applied to sheet resistance measurement data after implant anneal processes in a Rapid Thermal Processing system done on 200mm wafers.
The first method is developed to visualise "finger prints" of semiconductor equipment (e.g. Rapid Thermal Processor) on wafers. The second method is used to analyse preprocess homogeneity of process influencing parameters on the wafer. The third method investigates the metrology tool itself together with its lateral measurement error using only one test wafer.
Basis for the data processing is a standardised interface developed to import and analyse data files from different metrology equipment such as ellipsometers and four point probes.
- I-I.8** 12:10-12:30 **COUPLED SIMULATION OF GAS FLOW AND HEAT TRANSFER IN AN RTP-SYSTEM WITH ROTATING WAFER, S. Poscher, Fraunhofer Institut f. Integrierte Schaltungen - Bereich Bauelementetechnologie, Schottkystr. 10, 91058 Erlangen, Germany, and T. Theiler, STEAG- AST-Elektronik, Daimlerstr. 10, 89160 Dornstadt, Germany**
In this study the concept of a lamp heated RTP-system with rotating wafer is considered. Using the Fluid-Flow-Simulation software Phoenix-CVD we investigated the cooling of the wafer by a process gas flow which injected at room temperature into the hot process chamber through an inlet pipe in the side wall. In a full 3d-simulation of the gas flow and of the heat transfer in the gas and in the wafer the Navier-Stokes equations and the energy equation are solved. The radiative power consumption and the energy loss of the wafer have been modelled by the Stefan-Boltzmann law.
Simulations without wafer rotation show a strong drop in the temperature distribution at the wafer near the inlet pipe. In contrast to this simulations with rotation show an axisymmetric temperature distribution with a considerably smaller temperature gradient over the wafer. Comparisons with oxidation experiments proved good agreement with the simulation results. Further simulations were performed with a gas distribution plate in front of the inlet pipe. A distribution plate can decrease the inhomogeneity resulting from the inlet jet at a static wafer, but it has small effect on temperature homogeneity which can be received, when the wafer is rotating.
- 12:30-14:00 **LUNCH**

Tuesday June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-midi

SESSION II - Diffusion, shallow junctions & Activation
Chairperson: A. Timans, AG Associates, San Jose, USA

- I-II.1** 14:00-14:30 - Invited - **FREE CARRIER LIFETIME STUDIES & DOPANT DIFFUSION DURING RAPID THERMAL PROCESSING OF SEMICONDUCTORS, R.V. Nagabushnam*** and R.K. Singh, Dept. of Materials Science & Engineering, Univ. of Florida, Gainesville FL32611, USA, *currently at Advanced Products Research and Development Laboratory, Motorola, Austin, TX 78731, USA
Rapid thermal annealing of semiconductors involves significant photonic and subsequent thermal excitation. The photonic excitation has been speculated to lead to enhancement of dopant diffusion. In this work we present the experimental results reflecting the absence of any enhancement at high temperatures (~ 1000 to 1050 C) for the very important unit process of metal- oxide-semiconductor transistor manufacturing i.e. source/drain implantation anneal. To understand the effect of defects in controlling the diffusion process, the concentration of charged and neutral point defects have been calculated as a function of carrier concentration. The latter's dependence on lattice perturbation parameters such as impurities and temperature has been formulated and used in calculating point defect concentrations (C_v^* , C_i^*) and carrier lifetimes in semiconductor devices. Based on the obtained lifetimes, it appears that the carrier lifetimes are limited mainly by the equilibrium free carrier concentration (no) rather than the trap density (Nt) as the band to band Auger process seems to be the most dominant process.
- I-II.2** 14:30-15:00 - Invited - **CHANGING FROM RAPID THERMAL PROCESSING TO RAPID PHOTOTHERMAL PROCESSING: WHAT DOES IT BUY FOR A PARTICULAR TECHNOLOGY, R. Singh, V. Parihar, S. Venkataraman, K.F. Poole, Dep. of Electr. Eng. & Comp. Engineering and Centre for Silicon Nanoelectronics, Clemson University, Clemson SC 29634, USA; R.P.S. Thakur, AG Associates, San Jose CA95134; and A. Rohatgi, School of Electr. Eng., Georgia Inst. of Technology, Atlanta GA 30322, USA**
In recent years we have shown that rapid photothermal processing offers the following fundamental advantages over conventional rapid thermal processing: (i) reduced activation energy of the process, (ii) reduced processing time, and (iii) lower microscopic defects. The question remains to be answered that such a redesign of equipment will offer what extra mileage for a particular technology. Based on our extensive study of process integration and manufacturability (e.g., R. Singh, et.al., IEEE Trans. Elec. Dev., Vol 48, pp, 643-654, 1998) of silicon integrated circuits as well as the study of large area devices such as solar cells, we will demonstrate that as a thermal processing technique, RPP has the potential to meet manufacturing needs of every semiconductor product in the coming years. In this paper specific issues dealing with various semiconductor process technologies will be addressed.
- I-II.3** 15:00-15:20 **PHOSPHORUS DIFFUSION DURING RAPID THERMAL ANNEALING FROM A SOD SOURCE, D. Mathiot, A. Lachiq, S. Noël, A. Slaoui, and J.C. Muller, CNRS, Laboratoire PHASE (UPR 292), 23, Rue du Loess, B.P. 20, 67037 Strasbourg Cedex 2, France; C. Dubois, LPM, Bat. 502, INSA-LMyon, 69621 Villeurbanne cedex, France**
Limiting thermal exposure time using Rapid Thermal Processing (RTP) has emerged as a promising simplified process for microelectronic applications and for manufacturing of terrestrial solar cells in a continuous way. Especially, Rapid thermal diffusion (RTD) of phosphorus from doped oxide films (SOD) was extensively used for the emitter formation purpose but few work concerned the diffusion mechanism. Here we investigate more in details the diffusion kinetics of phosphorus after rapid thermal annealing of P-SOD coated silicon samples without or with an Al layer on the back side. Diffusion coefficients were deduced from phosphorus profiles and compared to those obtained after diffusion in a classical thermal furnace. The observed enhanced distribution of phosphorus after RTD is discussed based on the dopant sources and processing conditions. The effects of heating rates and thermal stress are considered.
- I-II.4** 15:20-15:40 **ULTRA-SHALLOW JUNCTION FORMATION BY RAPID THERMAL ANNEALING IN A FURNACE-BASED RTP SYSTEM, A. Agarwal, Eaton Corporation, Semiconductor Equipment Operations, 55 Cherry Hill Drive, Beverly MA 01915, USA; P. Frisella and J. Hebb, Eaton Corporation, Thermal Processing Systems, 2 Centennial Drive, Peabody MA 01960, USA**
This paper discusses the formation of 100 to 30 nm shallow p-type junctions from ultra-low energy (ULE) B⁺ implants by rapid thermal annealing in a furnace-based RTP system. The furnace-based system consists of a SiC bell jar which is resistively heated at the top and water-cooled at the bottom, establishing a vertical thermal gradient. Temperature of the wafer is determined by its vertical position within the furnace. Ramp rates of up to 80°C/sec are achieved by rapidly varying the wafer position. Data will be shown on the effect of the temperature ramp-up rate on dopant diffusion and activation in a hot wall furnace as well as a lamp based system. Specifically, the impact of ramp-rate on observed junction diffusion will be discussed in terms of the phenomenon of transient enhanced diffusion (TED).
- 15:40-16:10 **BREAK**

SESSION III - Silicidation

Chairperson: R.V. Nagabushnam, APRDL Motorola Inc., Austin, USA

I-III.1 16:10-16:40

CONTACTS TO SHALLOW JUNCTIONS USING TITANIUM SILICIDE WITH IN-SITU FORMED DIFFUSION BARRIERS, W. Zagodzón-Wosik, J. Li, I. Rusakova, S.R. Gooty, Z.H. Zhang, D. Marton, C. Lin, D. Simons*, P. Chi, R.J. Bleiler**, Electrical & Computer Engineering Dept, University of Houston, 4800 Calhoun, Houston, TX77204, USA; * NIST, Githsburg MD20899, USA; **Evans Texas, Austin TX78754, USA

We investigated process integration of shallow junctions formation and titanium silicidation, used as the contact layer. Junctions were doped with boron or arsenic in diffusion during rapid thermal processing (RTP). Dopant sources used in diffusion were in the form of pure B or As layers deposited on the silicon substrate by e-beam evaporation or molecular beam epitaxy (MBE), respectively. Contact formation to the junctions was preceded by Ti deposition either on a thin sacrificial layer of amorphous silicon or directly on the dopant source on silicon. We studied the role of dopant-metal compound formation as a diffusion barrier to prevent junction degradation during the silicidation process. Standard and modified RTP conditions were used for diffusion and silicidation processes including single steps for doping and contact formation in situ. Various analytical techniques (SIMS, AES, RBS, SRP) were used to determine dopant distributions in the junction and within the contact layers. Structure and crystallographic perfection were assessed by XTEM. Sheet resistance and contact resistance measurements were used to evaluate the processes.

I-III.2 16:40-17:00

EFFECT OF STRESS ON SILICIDE FORMATION KINETICS IN THIN FILM TITANIUM-SILICON SYSTEM, R.V. Nagabushnam* and R.K. Singh, Dept. of Materials Science & Engineering, Univ. of Florida, Gainesville FL32611, USA; currently at APRDL Motorola Inc., Austin TX78731, USA

As the CMOS device feature size scales below sub 0.5 μm , formation of low resistive C54 phase TiSi_2 becomes increasingly difficult. With the decreasing silicide thickness and shrinking line widths, unrealistic thermal budgets are required to transform the high resistive C54 phase. This phenomenon of sluggish C49 to C54 phase transformation, according to various researchers, has been attributed to the reduced nucleation density, i.e. relatively larger grained C49 phase formed as compared to the vertical and the lateral dimensions of the silicide.

Motivated by this technologically important C49 to C54 phase transformation, we have studied the ways in which a non thermal parameter such as "stress state", of the Ti-Si diffusion couple, could affect the silicide formation and the C49 to C54 transformation. The stress state of the Ti-Si diffusion couple was varied in three different ways: (i) stress state of the titanium film (ii) stress state of the silicon surface and (iii) use of an stressed overlying layer. We have observed that both the stress state of titanium film and the stress state of the silicon surface (modified by the ion implantation process) could significantly influence the C49 grain size. Specifically, both the compressive stress state of the Ti film and tensile stress state of the silicon surface results in smaller C49 grain size which leads to the enhanced C49 to C54 phase transformation. Similar such effects were observed for the experiments involving over lying layers of varying stress.

I-III.3 17:00-17:20

SILICIDATION AND ELLIPSOMETRIC CHARACTERIZATION, D.A. Tonova, J.E. Karmakov, A. Konova, Department of Condensed Matter Physics, Faculty of Physics, Sofia University, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria

Much work is devoted to understanding the basic mechanisms of the silicide formation and the associated reaction kinetics. The studies involve powerful but expensive surface-sensitive methods- XPS, RBS, SIMS, AES, REEM and TEMs.

For very thin films of metals, metallic alloys and silicides the spectroellipsometry is a sensitive tool for investigations. It gives some insight into reaction mechanisms of intermetallic layer growth and phase transformation during annealing. As an example we present our spectroscopic ellipsometry studies of evolution with time of CoSi_2 formation from thin Co film on silicon during RTA. Compositional profiles of cobalt silicide layer are determined by proper models and algorithms from ellipsometric data. Obtained results are consistent with the theory of grain boundary diffusion in thin polycrystalline films. Effective diffusion coefficient of moving species is determined.

I-III.4 17:20-17:40

STRAIN RELAXATION AND DOPANT DISTRIBUTION DURING THE RAPID THERMAL ANNEALING OF Co WITH $\text{Si/Si}_{0.8}\text{Ge}_{0.2}$ HETEROSTRUCTURES, Y. Miron*, M. Fastow*, C. Cytermann**, R. Brener**, M. Eizenberg*, **, *Department

of Materials Engineering and **Solid State Institute, Technion, 32000 Haifa, Israel and M. Glück, H. Kibbel, U. König, Daimler-Benz AG, Ulm Research Center, Germany

The reaction between Co and a sacrificial Si layer epitaxially grown on a strained SiGe epilayer is studied. The base structure consists of 600Å Si/ 400Å $\text{Si}_{0.8}\text{Ge}_{0.2}$ epitaxial layers MBE grown on a Si substrate. Some of the samples were ion implanted with B, and then RTA annealed for dopants activation. Co layers, 180Å and 100Å thick, were evaporated on the samples.

High Resolution X-ray and TEM analyses indicated that the structural quality of the implanted samples was very poor in comparison with the non-implanted samples. This may be attributed to the temperature of the activation annealing. The temperature was either too high and therefore caused strain relaxation; or it might have been too low, and therefore could not efficiently anneal the implantation damage. Silicidation was accomplished by RTA annealing at 550-700°C for 30sec. When the silicide penetrates the Si/ SiGe interface, as happens for the thicker Co layer, strain relaxation and diffusion of B and Ge toward the surface is observed. However, for the 100Å Co layer, the silicide is confined to the Si layer; resulting in negligible strain relaxation, and less segregation of B and Ge. Randomly distributed parallel squares, all in the same orientation, with a lateral dimension of 360nm, were observed by HRSEM. We suspect that these are epitaxial grains of CoSi_2 .

I-III.5 17:40-18:00

RAPID THERMAL ANNEALING OF Zr/SiGeC CONTACTS, M. Barthula, V. Aubry-Fortuna, O. Chaix-Pluchery*, F. Meyer, A. Eyal**, M. Eizenberg**, Institut d'Electronique Fondamentale, CNRS URA 22, Bât. 220, Université Paris Sud, 91405 Orsay Cedex, France; *LMGP, CNRS UMR 5628, ENSPG, BP75, 38402 St Martin d'Hères, France; **Solid-State Institute Technion, Haifa 32000, Israel

The fabrication of reliable ohmic and rectifying contacts is a critical step for novel $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ devices. The enhanced performances of heterojunction transistors are severely affected by dopant diffusion and strain relaxation that can occur during any thermal treatment. To reduce these detrimental effects, it is important first to reduce the thermal budget of contact formation by using Rapid Thermal Annealing (RTA) and second to choose a metal, such as Zr, which avoids Ge-segregation and the resultant strain relaxation. In this study, we have investigated the interface reaction and the electrical behavior of the Zr/ $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ contact as a function of the annealing temperature. The $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ ($x=10$ or 17% and $y=0$ or 1.3%) alloys were grown by RTCVD directly on Si substrates or on graded SiGe layers. Annealings were performed in a Rapid Thermal Annealing furnace under Ar/H_2 atmosphere for 5 min at 400, 600 and 800°C. The phase formation was followed by X-Ray diffraction and sheet resistance measurements. Four crystal X-Ray diffraction was performed to determine the residual strain and the lattice parameters of the unreacted SiGeC layer. The analyses indicated that the $\text{C49-Zr}(\text{Si}_{1-z}\text{Ge}_z)_2$ phase is the final phase of the reaction with $z=x$. We did not observe any Ge-segregation. In addition, the strain relaxation is always smaller than that observed in the Ti/SiGeC system and even does not occur in the SiGeC alloy. Schottky barrier heights (SBH) were determined by I-V measurements on p-type samples. The SBH on SiGeC is always larger than that on SiGe. We do not observe any degradation of the contacts after annealing. RTA at high temperature results only in a slight decrease of the SBH.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION IV - Dielectric Formation & Other Compounds

Chairperson: A. Tillman, STEAG AST Elektronik GmbH, Dornstadt, Germany

- I-IV.1** 14:00-14:30 - Invited - **ULTRA-HIGH TEMPERATURE RAPID THERMAL ANNEALING OF GaN**, X. Cao, R. Singh, **S.J. Pearton**, Department of Materials Science and Engineering, University of Florida, Gainesville FL 32611, USA; M. Fu and J.A. Sekhar, MHI, Cincinnati, OH 45212, USA; R.G. Wilson, Consultant, Winnetka, CA 92065, USA and J.C. Zolper, Office of Naval Research, Arlington VA 22217, USA
High dose ($>5 \times 10^{14} \text{cm}^{-2}$) Si^+ implants for creation of n^+ source/drain regions in GaN/AlGaN field effect transistors require activation annealing temperatures $\geq 1400^\circ\text{C}$. To minimize surface degradation, it is desirable to limit the thermal budget. We describe a novel RTP furnace based on molybdenum disilicide heating elements that is capable of reaching $\geq 1500^\circ\text{C}$ at high ramp rates. Activation percentages of $\sim 90\%$ for $5 \times 10^{15} \text{cm}^{-2}$, 100keV Si^+ implants were obtained after 1400°C annealing, corresponding to peak doping concentrations of $\sim 5 \times 10^{20} \text{cm}^{-3}$. Electron mobility is $40\text{--}50 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ under these conditions. Surface protection schemes based on provision of N_2 overpressures on AlN encapsulants were examined in the former case surface degradation occurs with an activation energy of $\sim 3.4 \text{eV}$ for GaN. SIMS measurements of Si redistribution show that $\text{D}_{\text{Si}} < 10^{-13} \text{cm}^2 \text{sec}^{-1}$ at 1400°C .
- I-IV.2** 14:30-14:50 **INFLUENCE OF VAPOR PHASE PRE-OXIDE-CLEANING ON THE OXIDATION CHARACTERISTICS**, B. Froeschle, N. Sacher, T. Theiler, STEAG-AST Elektronik GmbH, Daimlerstrasse 10, 89160 Dornstadt, Germany
As film thickness decreases, Si/SiO₂ interface properties play a more significant role with respect to gate dielectric processing and integrity. Thus, pre-gate surface preparation becomes one of the most critical steps in future device technologies. A cleaning process using anhydrous HF (AHF)/methanol is carried out in a Vapor Phase Cleaning module (VPC). This module is integrated in a state-of-the-art cluster tool also consisting of a Rapid Thermal Oxidation module (RTO). After the VPC step an additional cleaning step using ozone can be performed. The influence of the Pre-Oxide-Cleaning is investigated with respect to the subsequent oxidation in the RTO Module. Pure O₂ oxidation is compared to oxidation using N₂O or NO and oxidation with annealing in N₂, NO or N₂O. The chemical composition of the oxides is analyzed using Secondary Ion Mass Spectroscopy (SIMS). The wafer surface condition after the cleaning process is studied by X-Ray Photoelectron Spectroscopy (XPS). The results show the effects of different kind of surface conditioning on the oxidation characteristics.
- I-IV.3** 14:50-15:10 **RAPID THERMAL OXIDATION OF HIGHLY PHOSPHORUS DOPED POLYSILICON THIN FILMS**, S. Kallel, B. Semmache, M. Lemiti, A. Laugier, Laboratoire de Physique de la Matière, Bât 502, Institut National des Sciences Appliquées de Lyon, 20 Avenue Albert Einstein, 69621, Villeurbanne cedex, France
Ultra-thin oxides were obtained by RTO growth in a cold wall reactor using a pure dry O₂ (99.998%) atmospheric pressure. Heating is provided through a quartz window by a single bank of 12 tungsten-halogen lamps at process temperatures of 1000°C and 1100°C for a plateau time duration in the 5-100s range. Oxidation were carried out both on POCl₃-doped LPCVD polysilicon films and in-situ PH₃-doped RTLPVD polysilicon layers in order to point up the in-situ integrated multiprocessing offered by RTP treatments. RTO films thicknesses and refractive indexes were obtained by means of spectrometric ellipsometry. It has been noted that oxide growth rates are more accelerated when the temperature and/or phosphorus dopant concentration increases. Sheet resistivity measurements have shown that RTO process has a beneficial role for dopant activation. Besides, X-ray Photoelectron Spectroscopy (XPS) analysis revealed the presence of a substoichiometric oxide (SiO_x, $x < 2$) which is extended along 2 nm from the polysilicon/oxide interface. Finally, C(V) measurements indicated the good electrical quality of the polyoxide/polysilicon structure which can be advantageously used in MOS-integrated circuits and photovoltaic applications.
- I-IV.4** 15:10-15:30 **RAPID THERMAL OXIDATION OF POROUS SILICON FOR PASSIVATION PURPOSE**, L. Debarge, L. Stalmans*, J. Poortmans*, J.P. Stoquert and A. Slaoui, CNRS, Laboratoire PHASE, BP 20, 67037 Strasbourg cedex 2, France; *IMEC-MAP/PV, Kapeldreef 75, 3001 Leuven, Belgium
In this work, rapid thermal oxidation has been carried out on porous silicon (PS) films formed by electrochemical etching. The purpose was to investigate the surface passivation capability of the oxidized PS layers and to preserve the structure of the crystallites. The rapid thermal oxidation has been performed using a halogen lamps furnace unit with pure oxygen. The processing temperatures and times were varied from 700 to 900°C and from 5 to 120s, respectively. First analyses showed a decrease of the integral reflectance down to 5% for processing temperatures below 750°C revealing an anti-reflecting property of the RTO-PS layers although the porosity diminishes as proven by XTEM. On the other hand, Rutherford backscattering spectrometry (RBS) analysis confirmed the incorporation of a high amount of oxygen into the material and the formation of a quasi-silicon dioxide with the right stoichiometry. Besides, elastic recoil diffusion analysis (ERDA) demonstrated that a high concentration of hydrogen is still present in the PS film even after oxidation. This result is rather surprising as hydrogen is expected to out-diffuse from the material at 450°C , which is much lower than the oxidation temperature. Additional investigations will be presented.

15:30-16:00

BREAK

SESSION V - RTCVD Process

Chairperson: T. Theiler, STEAG AST Elektronik GmbH, Dornstadt, Germany

- I-V.1** 16:00-16:20 **DEPOSITION AND CRYSTALLIZATION OF a-Si THIN FILMS BY RAPID THERMAL PROCESSING**, S. Girginoudi, D. Girginoudi, N. Georgoulas, A. Thanailakis, Department of Electrical and Computer Engineering, Democritus University of Thrace, 67100 Xanthi, Greece and J. Stoemenos, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
The growth of poly-Si films is a crucial part in the fabrication of thin film transistor for flat panel display applications. In this work we have investigated the deposition and crystallization of a-Si thin films, grown by low-pressure rapid thermal chemical vapor deposition and subsequently annealed in situ by rapid thermal processing (RTP), using transmission electron microscopy. The deposition of a-Si was carried out in a cylindrical cold-wall rapid thermal reactor, using 20% silane diluted in argon in the temperature range 500-580°C for different deposition pressure and silane flow rates. The crystallization of a-Si films was achieved using single step high temperature RTA or double step RTA (low and high temperature RTA). The experimental results show that changes in the microstructure and surface roughness of poly-Si films with deposition conditions are strongly affected by the nucleation processes in the bulk of the films.
- I-V.2** 16:20-16:40 **THE INITIAL STAGES OF Si THIN DEPOSITS ON FOREIGN SUBSTRATES IN A THERMAL CVD-REACTOR**, D. Angermeier, R. Monna, S. Bourdais, A. Slaoui and J.C. Muller, CNRS-PHASE, 23 rue du Loess, 67037 Strasbourg, France
Nucleation and coalescence mechanisms of silicon clusters on silicon dioxide and high-purity alumina substrates have been investigated using rapid thermal chemical vapor deposition from SiHCl₃ diluted in a hydrogen carrier gas. The correlation between the formation of adatoms and the grain size evolution under various operational growth conditions were determined. In this respect, the saturation nuclei density, the further phases of clusters' enlargements and the formation of crystallites into a coalesced layer were taken into account. Additionally, the induction period for the establishment of the steady nucleation state, depending strongly on the supersaturation and on its preceding kinetics, was studied to characterize the activation process of the nucleus creation. Consequently, the physical properties of the used dissimilar substrates play a decisive role in the evaluation of the nucleation rate and the surface mobility of the clusters. Hence, a good Si film quality in terms of large grain sizes were obtained at elevated deposition temperatures and low chloride partial pressures.
- I-V.3** 16:40-17:00 **GROWTH AND PHYSICAL PROPERTIES OF IN-SITU PHOSPHORUS DOPED RTLCVD POLYCRYSTALLINE SILICON THIN FILMS**, S. Kallel, B. Semmache, M. Lemiti, A. Laugier, Laboratoire de Physique de la Matière, Bât 502, Institut National des Sciences Appliquées de Lyon, 20 Avenue Albert Einstein, 69621 Villeurbanne cedex, France and H. Jaffrezik, Métallurgie structurale, Ecole Centrale de Lyon, 36 Av. G. de Collonge, BP 163, 69131 Ecully, France
In-situ phosphorus doped polysilicon thin films are obtained by low pressure rapid thermal chemical deposition in a single chamber RTP machine by using diluted silane (SiH₄/Ar=10 %) and phosphine (PH₃=200 ppm). Deposition kinetics of polysilicon films have been studied in the 600- 850°C temperature range at fixed total pressure of 2 mbar and gas flow rate (100 sccm). An activation energy of 1.82 eV was measured in the surface reaction deposition regime. Dopant activation has been obtained sequentially by RTA at 1000°C in ² atmosphere. This later process permits to form an ultra-thin polyoxide which blocks the P-dopant outdiffusion. Secondary Ion-Mass Spectrometry (SIMS) analysis shows flat dopant profile throughout the film thickness with a dopant concentration varying from 5.5x10²⁰ cm⁻³ to 2.4x10¹⁹ cm⁻³ when the temperature increases in the 600- 850 °C range. Grazing incidence X-Ray Diffraction (XRD) has been used to study the structural and mechanical properties of the layers. It appears particularly that the amorphous to crystalline temperature transition occurs at around 650°C. Finally, four-point probe measurements have shown that sheet resistivities in the mΩ.cm range can be routinely achieved.
- I-V.4** 17:00-17:20 **OPTIMIZATION OF A TITANIUM NITRIDE RAPID THERMAL CHEMICAL VAPOR DEPOSITION PROCESS**, A. Bouteville, H. de Baynast, L. Imhoff, J.C. Remy, Laboratoire de Physico-Chimie des Surfaces, ENSAM - CER d'Angers, 2 Bd du Ronceray, BP 3525, 49035 Angers, France
For microelectronics devices, Chemical Vapor Deposition emerges as an interesting method for depositing titanium nitride layers as long as the thermal budget is kept low. By Rapid Thermal CVD, we obtained TiN layers of about 70 nm in thickness at a deposition temperature in the range 500 °C - 800 °C. However, we observed that the deposited thickness is not always proportional to the duration of the process. After a threshold, thickness drastically increases leading to deposit of poor density. The aim of this paper is to determine this threshold according to deposition parameters. Thanks to the fast response of the Rapid Thermal apparatus, well dense TiN layers can be obtained through an optimized process involving several short deposition steps.
- I-V.5** 17:20-17:40 **SIMULATION OF HEAT TRANSFER AND THERMAL STRESSES IN METALLIZED Si-SUBSTRATE UNDER RAPID INFRARED HEATING**, A.A. Dostanko, V.V. Baranov, A.A. Kostukevitch, I.N. Schukina, S.P. Kundas, D.N. Zwjagov, Belarus State University of Informatics and Radioelectronics, 6, P.Brovka Str., Minsk, 220027, Belarus
In microelectronics technology is broadly used the thermal treatment of silicon plates by means of pulsed infrared radiating. For computer investigation of this processes the numerical mathematical model of heat transfer and thermal stresses under rapid infrared heating of silicon plates was developed. The numerical algorithm of Si-substrate heating is based on finite-difference method of conduction equation solving (iteration Newton method). For description of the thermoelastic stresses distribution, appear as a result of nonstationary heat influences, not-bounded quasi-stationary problem of thermoelasticity applicable for two solid bodies was computed. For practical realisation of mathematical models a program complex was designed and temperature and thermal stresses distribution in silicon plates and metallized layers as function of heating time, co-ordinate and heating regimes were studied.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VI - Advanced Processing

Chairperson: S.J. Pearton, University of Florida, Gainesville, USA

- I-VI.1** 9:00-9:30 - Invited - **RAPID THERMAL PROCESSING AS A NEW EMERGING TECHNOLOGY IN FIELD-ANNEALING OF THIN MAGNETIC FILMS FOR RECORDING HEADS, F. Roozeboom**, Philips Research, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands; S. Abedrabbo and N.M. Ravindra, Dept. of Physics, New Jersey Institute of Technology, Newark NJ 07102, USA; H. Walk and M. Falter, Steag-AST Elektronik, Daimlerstrasse 10, 89160 Dornstadt, Germany
A new emerging field where RTP is rapidly finding its first acceptance in industrial manufacturing of thin-film head devices for magnetic recording. Here the thin-film structures (usually composed of iron or cobalt alloys) are applied onto ceramic substrates (Mn-Zn ferrite and $\text{Al}_2\text{O}_3\text{-TiC}$) of sizes up to 150 mm, and subsequently heated and cooled in a magnetic field. These substrate materials have favorable grey-body properties with high emissivity (≈ 0.7) over a wide wavelength range. Temperature homogeneity is as important here as in the semiconductor industry: the temperature deviation across a 150 mm wafer should not exceed $\pm 5^\circ\text{C}$ to keep the magnetostriction constant of the thin magnetic films within the specification of mass-manufacturing of thin-film heads ($< 2 \times 10^{-7}$). We assessed the advantages of RTP field annealing in a new prototype reactor with an external electromagnet generating an extremely homogeneous magnetic field across the entire wafer area (150 mm in diameter). Samples with sputter-deposited 1 μm thick amorphous iron-alloy layers ($\text{Fe}_{77}\text{Nb}_{11}\text{N}_{10}\text{Si}_2$) were RTP-annealed in N_2/H_2 . Conventional annealing was done in a vacuum oven. Structural analysis by TEM showed that the enhanced performance of the RTP-annealed layers is due to the different crystallization kinetics induced by the fast heating and cooling rates of RTP. Throughput numbers of 20-30 wafers / hour are possible.
- I-VI.2** 9:30-10:00 - Invited - **EPITAXIAL GROWTH OF Si-Ge LAYERS FOR ULSI APPLICATIONS, J.L. Regolini**, T. Baffert, J. Pejnefors, C. Morin, M. Marty*, A. Chantre and T. Skotnicki, FRANCE TELECOM-CNET Grenoble, 28 Ch. Du Vieux Chêne, 38243 Meylan Cedex, France; *SGS-Thomson, BP 16, 38921 Crolles Cedex, France
Silicon-germanium materials introduced the opportunity to engineer the energy band gap of Si leading to a wide range of microelectronic device applications. The growth of high quality Si-Ge layers by Chemical Vapor Deposition at reduced temperature and pressure has already been reported from our GRESSI Program. In addition to those results we have studied the stability of Si-Ge strained layers to be used as the base of HBTs or the channel of MOS structures. Indeed, layer growth conditions such as temperature, Ge content, selectivity/non selectivity may induce structural defects as misfit dislocations, thus giving as a result leaky devices and less performant ICs. Using an industrially available CVD single wafer reactor we have fabricated and studied Si/SiGe stacks for CMOS and BiCMOS applications. The obtained electrical results are correlated with the growth parameters and structural observed defects in order to optimise device characteristics and process windows.
- I-VI.3** 10:00-10:20 **STRUCTURAL TRANSFORMATION IN BULK GaAs AND STRUCTURES UNDER MICROWAVE TREATMENT, T.G. Kryshtab, O.S. Lytvyn, P.M. Lytvyn, I.V. Prokopenko**, Institute of Semiconductor Physics, National Academy of Sciences of the Ukraine, 45 Nauki prospect, 252028 Kiev, Ukraine
The structural relaxation processes in various bulk GaAs and GaAs-based structures under microwave electromagnetic irradiation (2,38 GHz) depending on power (2 and 5 kW) and duration (minutes and seconds) of treatment were investigated. By X-ray diffraction methods were observed the changes of the structural characteristics, such as: residual strains, stoichiometry, inclusions, dislocations, growth striations. The structural relaxation processes in GaAs substrates and structures stimulated by microwave electromagnetic field irradiation in time and after its finishing are determined by complex interaction of the thermal, electrical and mechanical phenomena. The character and ratio of these phenomena depend on the initial structural perfection of the exposed material, its morphological parameters and processing conditions. The kinetics of relaxation processes after strong microwave irradiation of substrates and structures has long duration non-monotonous character, i.e. dislocation-point defect balance is not achieved and mechanism of interaction between the high-power microwave radiation and semiconductor, generally, has strongly non-equilibrium character. Nevertheless, when the optimum annealing conditions are selected, microwave processing can be used as technological annealing for improvement structural uniformity of substrates and structures with stable parameters.

10:20-11:00

BREAK

SYMPOSIUM I

SESSION VII - Solar Cells & Large Area Devices

Chairperson: N.M. Ravindra, University Heights, Newark, USA

I-VII.1 11:00-11:20

SURFACE MODIFICATIONS IN Si AFTER RTA, E. Susi, A. Cavallini*, A. Castaldini*, CNR, Istituto LAMEL, via Gobetti 101, 40129 Bologna, Italy; *Dipartimento di Fisica and INFN, Università di Bologna, Italy

The objective of our work is the study the electrical properties of the Si wafers and to monitor the modifications in these properties due to the processing.

In this work we report the results of a study of the modifications in the surface and bulk properties of p-type Si wafers after a lamp annealing at 750 and 1050°C. We have used different experimental techniques: current-voltage (I-V) and capacitance-voltage (C-V) characteristics of Schottky diodes, deep level transient spectroscopy (DLTS), surface recombination velocity measurements and the electron beam induced current (EBIC) mode of a scanning electron microscope (SEM). This technique allows a direct imaging of the recombining defects, and, from the analysis of the spatial distribution of the induced current, a calculation of local surface recombination velocity. From the correlation with the macroscopic value of surface recombination velocity a direct monitoring of the recombination behavior of the studied surface is possible, and, therefore, useful information on the electrically active defects responsible of the modification of the surface properties can be obtained.

The most important effects of the annealing is the increase of the surface recombination characteristics. The effect is lower than in n-type Si [1]. The correlation with the defects observed by EBIC and the deep levels detected by DLTS and the dependence on the quality of the starting wafers are discussed.

[1] E. Susi, A. Poggi, M. Madrigali, J. Electrochem. Soc., 142, 2081, (1995).

I-VII.2 11:20-11:40

SELECTIVE DOPING OF SILICON BY RAPID THERMAL AND LASER ASSISTED PROCESSES, L. Pirozzi, U. Besi Vetrella, E. Salza, S. Noël*, A. Slaoui* and J.C. Muller*, ENEA Casaccia, Via Anguillarese 301, 00060 Roma, Italy; *PHASE-CNRS, 23 rue du Loess, 67037 Strasbourg, France

The selective doping technique, made by the combination of Spin-On Dopant (SOD) source deposition, Rapid Thermal Annealing (RTA), and laser treatments, is a very innovative process for many applications in large area devices, such as, for example, the silicon solar cells.

Regions with different doping profiles are achieved by over-doping by laser previously RTA diffused layers. The over-doping is obtained by laser, which melts the surface of the substrate and induces, in the same time, the diffusion of dopant atoms from the dopant source.

In this paper we present results on selective doping characteristics of Silicon as a function of different working variables. The parameters which have been changed are the thickness of the Spin-On-Diffusant (SOD) film, the RTA temperatures and time, as well as the laser properties like power, repetition rate and substrate translation velocity.

The junctions properties were evaluated by SIMS and Stripping-Hall techniques, I-V curves and four-point sheet resistance measurements. The results were correlated to the different experimental conditions.

Moreover recrystallization after the laser melting has been monitored by SEM and TEM analyses showing, in most cases, very well re-grown, defect free regions.

Furthermore, we have optimized the selective doping technique for the realization of selective emitter structures n+/n in high efficiency silicon solar cells.

I-VII.3 11:40-12:00

RAPID THERMAL ANNEALING APPLIED TO THE OPTIMIZATION OF TITANIUM OXIDE ARC, M. Lemiti, J.P. Boyeaux, H. El Omari, A. Kaminski and A. Laugier, Laboratoire de Physique de la Matière, UMR 5511, INSA de Lyon, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France

The aim of this study is the development of an antireflective coating (ARC) technique for large multicrystalline solar cells with a high throughput capability. The technique used for high production rate and low cost coating process is the atmospheric pressure chemical vapor deposition (APCVD) at low temperature, in order to keep porosity of layers. If the thin passivating SiO₂ layer and the encapsulated layer are taken into account, the value of index to be reached is 2.4 for an ARC thickness of 70 nm. Rapid thermal annealing (RTA), performed in air in order to facilitate the industrial use, and in 400°C - 700°C range, are used to adjust simultaneously index and thickness of layers.

On one hand, titanium dioxide films are deposited on silicon wafers at 160°C from hydrolysis of titanium isopropoxide (TPT). We have obtained refractive indexes of 1.8 - 1.9 with a layer thickness of 100 nm in order to anticipate the thickness decreasing which occurs during thermal treatments necessary to solar cells fabrication. After annealing during 120 s at 700 °C, the refractive index is 2.25 and thickness is 60 nm.

On the other hand, thin TiO₂ films are produced at 150 °C using the hydrolysis of TiCl₄: we have investigated this way in order to achieve a higher optical index associated to a fast deposition rate. The refractive index is 2.1 - 2.3 as deposited and the thickness in the range 70 - 90 nm. All films are amorphous as grown. After annealing during 120 s at 700 °C, the index increases until 2.4 with a beginning of anatase phase verified by X rays diffraction and the thickness decreases by 15%.

In conclusion, we can obtain industrial oxide layers with adjustable index.

I-VII.4 12:00-12:20

RAPID THERMAL PROCESSING OF PRINTED OHMIC CONTACTS FOR SILICON SOLAR CELLS, P. Hahne, D. Huljic, I. Reis, Fraunhofer-Institut für Solare Energiesysteme ISE, Oltenstr. 5, 79100 Freiburg, Germany

At Fraunhofer ISE printed ohmic contacts on solar cells are fired with Rapid Thermal Processing (RTP). In comparison to conveyor belt furnaces process parameters, such as gas atmosphere and temperature ramps, can be easily adapted to different types of silver pastes, which are under investigation.

By using a test structure the firing conditions with RTP were optimised to improve the electric properties of silver front contacts such as resistivity of the fired paste and contact resistance of the silver/silicon-interface. Optimisation has been carried out by using proved methods like Design of Experiment (DOE) and Response Surface Methods (RSM). The knowledge obtained was applied to firing of multicrystalline solar cells. Results will be presented.

Further on, influences of firing conditions on the silver/silicon-interface were investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM), the structure of different fired pastes were investigated by x-ray diffraction (XRD).

12:20

LUNCH

END OF SYMPOSIUM I

E-MRS'98 SPRING MEETING



SYMPOSIUM J

Ion Implantation into Semiconductors, Oxides and Ceramics

Symposium Organizers

- J.K.L. LINDNER** Universität Augsburg, Augsburg, Germany
- P.L.F. HEMMENT** University of Surrey, Guildford, UK
- H.A. ATWATER** California Institute of Technology, Pasadena, USA
- B. SVENSSON** Royal Institute of Technology, Kista-Stockholm, Sweden

The assistance provided by

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Danfysik Eaton

is acknowledged with gratitude.

(The Netherlands)

(USA)

SYMPOSIUM J

Tuesday, June 16, 1998

Mardi 16 juin 1998

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8:40-8:45

OPENING SESSION

SESSION I - Group IV Semiconductors, Part 1

Chairpersons: S. Coffa, CNR-IMETEM, Catania, Italy

J. Lindner, Universität Augsburg, Institut für Physik, Augsburg, Germany

- J-I.1** 8:45-9:15 - Invited - **NUCLEATION GROWTH AND DISSOLUTION OF EXTENDED DEFECTS IN IMPLANTED Si: IMPACT ON DOPANT DIFFUSION**, **A. Claverie**, L.F. Giles, M. Omri, B. de Mauduit, G. Ben Assayag and C. Bonafos, CEMES/CNRS, BP 4347, 31055 Toulouse Cedex, France
Transient Enhanced (or Retarded) Diffusion of dopants generally occurs during the early stages of the activation anneals. This phenomenon is observed both after "direct" implantation in crystalline Si and after the surface wafer has been amorphized prior to dopant implantation. In both cases, these "diffusivity" anomalies are due to the time and space evolutions of the Si interstitial supersaturations that result from the implantation. On the other hand, in most of experimental situations in which TED is observed, extended defects of interstitial type are also formed which also evolve in types, sizes and densities upon annealing. In this paper, we will review our current knowledge of defect nucleation, competitive growth and eventual dissolution upon thermal annealing of a supersaturated medium. We will show that the kinetic behavior of these defects does reflect the concomitant evolution of the Si self-interstitial supersaturation in the region and responsible for TED. However, many questions still remain concerning the "propagation" of this supersaturation in the bulk and toward the surface as well as the recombination efficiencies of the surface and interfaces. These questions will be identified and discussed.
- J-I.2** 9:15-9:30 **MODELISATION OF THE KINETICS OF DISLOCATION LOOPS**, **E. Lampin**, V. Senez, IEMN, Avenue Poincaré, B.P. 69, 59652 Villeneuve d'Ascq Cedex, France
Preamorphization of silicon permits to avoid the boron channeling at implantation. This is a condition required for VLSI technology to obtain shallow junctions. The amorphization is commonly achieved by Si or Ge implantation. These heavy ions create damages in the silicon substrate: amorphization at the surface and great supersaturation of interstitials just beneath the interface amorphous/crystalline. During the annealing necessary to re-establish the crystalline structure, these silicon interstitials may precipitate into dislocation loops, as it has been experimentally evidenced[1]. A modelisation of the kinetics of the interstitials precipitation into dislocation loops is presented. The nucleation rate is written as a steady state one, reached after an incubation time, and the growth rate of an average precipitate is assumed to be limited by the diffusion of the interstitials. These two rates allow to describe the evolution of the interstitials trapped in the loops. The numerical resolution is made thanks to the implementation of the model into our process simulator IMPACT-4. A second stage, Ostwald ripening, is also incorporated in the model. The evolution with annealing time and temperature of the mean radius and the concentration of the dislocation loops is in good agreement with the experiments.
[1]A. Claverie et al., Nucl. Inst. and Meth. in Phys. Res. B96, 202(1995).
- J-I.3** 9:30-9:45 **REACTIVE PLASMA ETCHING: A NOVEL METHOD TO REDUCE TRANSIENT ENHANCED DIFFUSION OF LOW ENERGY IMPLANTED BORON IN SILICON**, **G. Mannino**, F. Priolo, INFN and Dipartimento di Fisica, Catania, Italy and V. Privitera, IMETEM (CNR), Catania, Italy
We present a novel method to reduce transient enhanced diffusion (TED) of low energy implanted boron in silicon. By means of plasma etching processing the TED phenomena are strongly reduced. We observed that the near-surface plasma-induced extended defects act as trapping centres for the interstitials generated by B implants (3-5 keV). Moreover, we found that the TED reduction depends critically on the implant projected range. An extensive characterisation of defects induced by plasma was done both in terms of evolution, trapping capability and interaction distance with point defects. Several plasma conditions have been used and their impact on the reduction of TED has been characterised. The role of carbon, often contained in standard plasma to etch oxide, was investigated. Due to the standard use of reactive plasma etching for device fabrication, this defect/diffusion engineering procedure represents a promising approach to TED suppression and might have important potential applications for ultra-shallow (< 1000Å) junction formation.

J-I.4 9:45-10:00

MIGRATION AND INTERACTION PROPERTIES OF ION BEAM GENERATED POINT DEFECTS IN c-Si, S. Libertino and S. Coffa, CNR-IMETEM, Stradale Primosole 50, 95121 Catania, Italy

Quantitative information on room temperature properties of interstitials (I) and vacancies (V) are precious for the comprehension and modeling of defect accumulation in ion implanted crystalline Si. Experimental assessments of fundamental properties such as I and V diffusivities are difficult to interpret since the role played by defect trapping at dopants (B or P) and at impurities (O, C), as well as ionization enhanced migration phenomena need to be disentangled. The aim of this work is to obtain new insights on these phenomena. Deep level transient spectroscopy (DLTS) measurements were used to monitor the depth profiles of electrically active V-type (such as VV and OV) and I-type (P_0C_0 and B_0C_0) defect complexes generated by He (1-3 MeV, 1×10^{10} - $5 \times 10^{11} \text{ cm}^{-2}$) or Si (0.04-3 MeV, 1×10^{10} - $5 \times 10^{12} \text{ cm}^{-2}$) implantation. P-type or n-type Si samples with impurity content in the range $\sim 2 \times 10^{15}$ - $1 \times 10^{18} \text{ cm}^{-3}$ were used. The results prove that both V and I exhibit fast long range migration at room temperature which is interrupted by trapping at impurities, dopant atoms of other defects. Moreover, it is shown that the analysis of the introduction rate of I-related complexes allows to evaluate impurity content at levels not detectable with traditional techniques. Finally, in-situ conductivity measurements on damage evolution of ion damage on p-type, n-type and depletion layers of a p-n junction will be presented and used to assess the role of defect charge state on migration

J-I.5 10:00-10:15

DEFECTS IN a-Si-IMPLANTED a-Si:H FILMS DEPENDING ON THEIR INITIAL PARAMETERS, O.A. Golikova, M.M. Kazanin, A.F. Ioffe Institute, 194021 St. Petersburg, Russia

A-Si:H films implanted with Si ions ($\epsilon = 60 \text{ keV}$, $D = 10^{11}$ - 10^{13} cm^{-2} , $T = 300\text{K}$) have been investigated. They were deposited by rf-PECVD and by the dc-MASD [1] at T_s -200-350°C. These techniques ensured the changes in Fermi level position ($\epsilon_c - \epsilon_F = 0.7$ -1.0 eV) determining the defect density, N_D , and charge state (neutral, D^0 , or negative, D^-) in nominally undoped a-Si:H [2] as well as the changes in H content (5-10 at.%), type of Si-H bonds (isolated SiH and SiH_2 , $(\text{SiH})_n$ clusters) and their contribution characterized by the microstructure parameter ($R=0$ -0.75). The investigation techniques were described elsewhere [1]. The following Si-implantation induced effects have been observed: the N_D growth, the ϵ_F shifts toward the c-band at the lowest dose and its achieving the midgap with increasing dose, H effusion. Each of them were shown to depend on the initial parameters of the films. The data obtained enable us to conclude that the ion beam interaction with a-Si:H can lead to changes in the defect charge ($D^0 \rightarrow D^-$), to ruptures of weak Si-Si and also Si-H bonds that results in N_D up to 10^{17} cm^{-3} and 10^{19} cm^{-3} , respectively.

[1] O.A. Golikova, A.N. Kuznetsov, V.Kh. Kudoyarova, M.M. Kazanin. Semiconductors 29, 299, 1995.

[2] O.A. Golikova. Semiconductors 31, 228, 1997

10:15-10:45

BREAK

SESSION II - Group IV Semiconductors, Part 2

Chairpersons: **J. Lindner**, Universität Augsburg, Institut für Physik, Augsburg, Germany

S. Coffa, CNR-IMETEM, Catania, Italy

J-II.1 10:45-11:15 - Invited -

STRAIN RELAXATION OF EPITAXIAL Si-Ge-LAYERS ON Si IMPROVED BY HYDROGEN IMPLANTATION, S. Mantl, R. Liedtke, B. Holländer, St. Mesters, Institut für Schicht-und Ionentechnik, ISI-IT, Forschungszentrum Jülich, 52425 Jülich, Germany, H.-J. Herzog, H. Kibbel and T. Hackbarth, Daimler Benz Forschungsinstitut Ulm, 89013 Ulm, Germany

We propose a new way to fabricate strain-relieved epitaxial Si-Ge-layers with a low threading dislocation density on Si(100) by hydrogen implantation and thermal annealing. Pseudomorphic $\text{Si}_{1-x}\text{Ge}_x$ layers on silicon are elastically strained due to the lattice mismatch of up to 4% for pure Ge on Si. However, strain-relieved Si-Ge-layers with Ge concentrations >20 at% are highly desired for ultrafast Si-Ge devices. We investigated the effect of hydrogen implantation into fully strained Si-Ge layers with Ge concentrations in the range of 10 to 25 at%, followed by annealing. The pseudomorphic layers with thicknesses of $\approx 200 \text{ nm}$ were grown by molecular beam epitaxy on Si(100). These layers were implanted with $3 \cdot 10^{16} \text{ H}^+ \text{ cm}^{-2}$ at an energy of $\approx 25 \text{ keV}$. Annealing causes first the formation of hydrogen bubbles and at higher temperature ($> 1000^\circ\text{C}$) complete strain relaxation of the originally pseudomorphic Si-Ge layers. Surprisingly, cross-sectional transmission electron microscopy revealed a defect band below the heterointerface, but no threading dislocations in the Si-Ge-layer. Planar ion channeling confirmed those findings. X-ray diffraction showed that the implanted and annealed sample is strain relaxed.

J-II.2 11:15-11:30

FORMATION OF EXTENDED DEFECTS AND STRAIN RELAXATION IN ION BEAM SYNTHESISED SiGe ALLOYS, F. Cristiano, A. Nejim and P.L.F. Hemment, School of Electronic Engineering, University of Surrey, UK; Yu. Suprun-Belevich, Department of Physics of Semiconductors, Belarusian State University, Minsk, Belarus and A. Claverie, CEMES-LOE/CNRS, BP 4347, Toulouse, France

Single crystal SiGe alloy layers have been fabricated by implantations of Ge^+ ions at energies ranging from 70 keV to 400 keV, with and without Si^+ post-amorphisation, followed by SPEG. The germanium content in the alloys was determined by RBS, while TEM and XRD analysis have been used to investigate the formation of extended defects and the relaxation state of the various structures, respectively.

For each Ge^+ implantation energy a critical value of the peak germanium concentration exists above which extended defects (stacking faults and/or "hairpin" dislocations) nucleate in the vicinity of the peak of the germanium depth profile and extend up to the surface. A critical value of the elastic energy stored in the structures ($\sim 300 \text{ mJ/m}^2$) has been determined above which ion beam synthesised SiGe alloys relax, independently of the implantation energy. This empirical approach has been found to successfully account for the results obtained in this work as well as in many other studies reported in the literature. For a regrowth temperature of 700°C , all samples investigated by XRD have been found to be almost fully strained, including samples containing relaxation-induced defects, indicating that, under these conditions, the energy transferred to the defects is very low. Complete strain relaxation is achieved after a second anneal step at 1000°C . A model to describe this behaviour will be presented.

J-II.3 11:30-11:45

SiGe-ON-INSULATOR SUBSTRATE FABRICATED BY LOW ENERGY OXYGEN IMPLANTATION, Y. Ishikawa, T. Saito and N. Shibata, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta, Nagoya 456-8587, Japan; S. Fukatsu, Department of Pure and Applied Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

In this paper, we report successful approach toward SiGe-based SOI.

SiGe-based semiconductor-on-insulator (SOI) substrates have attracted much attention since record electron mobility has been reported recently by growing a tensilely-strained Si channel on top of a strain-relaxed SiGe. In the field of optics, a high refractive index step at the SiGe/SiO₂ interface promises a good reflector.

In this experiment, 25keV O⁺ implantation was performed on a SiGe virtual substrate at 550°C followed by ex.situ annealing at 1280°C for 6 hours in N₂. Dislocation-free, fully-relaxed starting substrates were created by growing Si_{0.82}Ge_{0.18} on top of a 9-step compositionally graded Si_{1-x}Ge_x buffer (x=0-0.18) on Si(001). Transmission electron microscopy and energy dispersive spectroscopy were performed for the characterization of morphological features as well as compositional profile. The SIMOX (dislocation- and island-free) is obtained within the dose window of 2-2.5x10¹⁷/cm² while parasitic SiGe islands are formed in the buried oxide beyond this window. The top SiGe layer conserves the same composition as the starting alloy substrate. The buried oxide has turned out to be Ge-free. Compositional transients of Ge and O are abrupt across the interface. Sharp SiGe/SiO₂ interfaces are also confirmed by lattice imaging. We further demonstrate that an ultra thin, dislocation-free SiGe-SIMOX is accessible by starting with a normal compressively strained SiGe/Si(001). This offers a low cost and high throughput SiGe-SIMOX process.

J-II.4 11:45-12:00

TEM STUDIES OF THE DEFECTS INTRODUCED BY ION IMPLANTATION IN SiC, J. Grisolia, B. de Mauduit, J. Gimbert*, Th. Billon*, G. Ben Assayag, C. Bourgerette and A. Claverie, CEMES/CNRS, BP 4347, 31055 Toulouse, France; *LETI/CEA, Centre d'Etudes Nucléaires, 38054 Grenoble Cedex 9, France

In SiC, doping by ion implantation has been shown to be much more difficult than in Si. The reasons for the rather small activations one obtains even after high temperature anneals are not all understood and the role of the extended defects which are formed is not established. For this reason, we have undertaken a systematic characterization (40 samples) of the defects formed by ion implantation in SiC for a large variety of experimental conditions. B, N, Al and Ne ions were implanted in 6H-SiC at room temperature and at 650°C. Mono-implants or multi-implants were carried out in order to obtain "flat" dopant profiles and the samples were annealed from 1300 to 1700°C for various duration times. TEM analysis of these samples was carried out on cross-sectional samples using Weak Beam Dark Field imaging conditions. A statistical analysis of digital images was performed to extract the depth-distributions of the defects. All these defects are of interstitial type (clusters or loops). These depth-distributions have been compared with MC simulations of the ion implantation process. It is shown that when implanted at RT, the defect distributions follow the "damage" profiles i.e. defects appear where atomic displacements occur in the target. In contrast, the defects found after implantation at 650°C always mimics the "range" profile and this before and after annealing. We show that there is a concentration threshold under which no defect appears. These results will be discussed in terms of point defect annihilation, clustering and dopant activation in SiC.

J-II.5 12:00-12:15

ELECTRONIC STOPPING POWER FOR MONTE CARLO SIMULATION OF ION IMPLANTATION INTO SiC, E. Morvan, P. Godignon, S. Berberich, M. Vellvehi, J. Millán, Centro Nacional de Microelectronica (CNM-CSIC) Campus UAB,08193 Bellaterra, Spain

Ion implantation is the only process which allows selective doping of SiC. Advanced processes such as high energy multiple implantations for deep junction formation or compensating implants for device isolation or edge termination of power devices have been used successfully. Coinplantation with Si or C also gave promising results in term of dopant activation for contact-technology and low sheet resistance layers. A Monte Carlo (MC) simulator is usefull for optimizing multiple implants and investigating damage formation or channeling. Such a simulator has been developed at CNM. The ability of the simulator to predict implanted dopant profiles relies on the validity of the physical models involved. One of the most critical model for MC-calculations is the Electronic Stopping Power (ESP) model which gives the energy loss of an ion due to its interaction with the electrons of the crystal. Various ESP models have been used for implantation simulation into Si. In this paper we compare four ESP models for Al into 6H-SiC: the Lindhart & Scharff model, the TRIM simulator model, the semiempirical local/nonlocal model based on the impact parameter dependent formula of Oen & Robinson and a new model based on the non linear density functional formalism of Etchenique and the electronic density calculations of Park. Confrontation of simulations with measured SIMS profiles evidences the superiority of the new model. The Al impurity has been choosen for the sensitivity of the Al profile on ESP. This study is also applied to other dopants in SiC.

J-II.6 12:15-12:30

DOPING OF 6H-SiC pn STRUCTURES BY PROTON IRRADIATION, A.A. Lebedev, A.M. Strel'chuk, N.S. Savkina, D.V. Davydov, A.F. Ioffe Physico Technical Institute, Polytechnicheskaya 26, St. Petersburg, Russia and V.V. Kozlovski, St. Petersburg State Technical University, Polytechnicheskaya 29, St. Petersburg, Russia

The influence of proton irradiation on current-voltage characteristics, N_d-N_a value and parameters of deep centres in 6H SiC pn structures ($N_d-N_a = 4 \cdot 10^{16} \text{ cm}^{-3}$) grown by sublimation epitaxy has been studied. Irradiation with 8 MeV protons was performed on a MGTs-20 cyclotron at doses in the range $10^{14} - 10^{16} \text{ cm}^{-2}$. First, irradiation with doses lower than $3 \cdot 10^{14}$ leaves practically unchanged the resistance of pn structures. Second, with increasing irradiation dose, the resistance and degree of compensation in samples increases. DLTS studies have shown that irradiation causes, in addition to an increase in the concentrations of R-centre and Z1/Z2 centre previously observed in CVD-grown 6H SiC layers, formation of new centres in the lower half of the forbidden gap and also increases the concentration of the D centre. Partial annealing of radiation defects and also partial restoration of electrical parameters on pn structures subjected to proton irradiation occurs after annealing at T~500°C. Finally, irradiation with doses $>5.4 \cdot 10^{15} \text{ cm}^{-2}$ results in the very high resistance of the forward biased pn structures and resistance remain high even after heating to 500°C. These investigations show that radiation doping is promising way to obtain high resistivity silicon carbide layers. This work was partly supported by Arizona University and Schneider Group Research centre.

12:30-14:00

LUNCH

Tuesday, June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III - Ion Implantation for Optical Applications, Part 1

Chairperson : A. Claverie, CEMES-CNRS, Toulouse, France

- J-III.1** 14:00-14:30 - Invited - **ION IMPLANTATION DOPING OF CRYSTALLINE Si FOR OPTOELECTRONIC APPLICATIONS**, S. Coffa, G. Franzó, CNR-IMETEM, Catania, Italy and F. Priolo, INFN and Dipartimento di Fisica, Catania, Italy
For several present and future applications in the field of communication technologies, photonic materials, in which light can be generated, guided, modulated, amplified and detected, need to be integrated with standard electronic circuits in order to combine the information-processing capabilities of electronics and the data-transfer speed of light. Due to its indirect bandgap Si, the leading semiconductor in the electronic arena, is unable to exhibit efficient light emission and has been considered unsuitable for optoelectronic applications. In this talk, rare-earth doping (Er, Tm, Ho, etc.) of crystalline Si by ion implantation is proved to be a successful approach to achieve efficient light emission from Si. The role of ion beam damage and impurity codoping on the structural, electrical and optical properties of rare earth ions in Si will be elucidated. The results of a detailed investigation of the carrier-mediated excitation and de-excitation mechanisms for these ions in c-Si and a-Si:H will be presented. The proper tuning of the material properties and an optimized device structure are shown to result in room temperature operating Er-doped Si LEDs having efficiency of ~ 0.1% and modulation bandwidth of ~ 10 MHz. The integration of the Er-doped Si LEDs with Si waveguides and electronic functions on the same chip will also be presented and the perspectives of a fully Si-based optoelectronics evaluated. Finally, rare earth doping will be compared to other approaches to light emission using ion beams, such as the synthesis of β -FeSi₂.
- J-III.2** 14:30-14:45 **OPTICAL AND ELECTRICAL CHARACTERIZATIONS OF Mn DOPED P-TYPE β -FeSi₂**, T. Takada***, Y. Makita*, T. Banba***, K. Shikama, H. Sanpei, M. Hasegawa*, A. Sandhu, Y. Hoshino***, H. Katsumata**** and S. Uekusa**; Tokai University, 1117 Kitakaname, Hiratsuka 259-1207, Japan; *Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan; **Meiji University, 1-1-1 Higashi-mita, Tama, Kawasaki, Kanagawa 214-0033, Japan; ***Nippon Institute of Technology, 4-1 Gakuendai, Miyashiro, Minamisaitama 345-0826, Japan; ****Kyoto University, Sakyo, Kyoto 606-8317, Japan
 β -FeSi₂ has attracted increasing attention as a promising material for optoelectronic devices and thermoelectronic devices due to a high optical absorption coefficient (α) of about 10^5 cm^{-1} near 1.0 eV and its chemical stability at higher temperatures. For the future practical use of this material as these devices, the control of each electrical conductivity type and the improvement of the material quality are highly required. Although unintentionally doped β -Fe Si₂ layers formed on n-type Si(100) by simple electron beam deposition (EBD) have typically shown n-type conductivity, the p-type β -Fe Si₂ layers were formed by both the introduction of Mn impurity using ion-implantation at room temperature (R.T.) and subsequent annealing procedures. In this study, we aim to make p-type β -Fe Si₂ by implantation of $^{55}\text{Mn}^+$ ions into EBD-grown n-type β -Fe Si₂ layers/n-Si, where $^{55}\text{Mn}^+$ ions were implanted at two different temperatures (T_{sub}) of R.T. and 250°C using an energy and a dose of 300 keV and $2.68 \times 10^{15} \text{ cm}^{-2}$, respectively. Their optical and electrical properties, which could be affected by implantation and annealing temperatures (T_{a2}), were investigated by Raman Scattering, optical transmittance, reflectance and van der Pauw measurements. The results showed that the $^{55}\text{Mn}^+$ doping with $T_{\text{sub}} = \text{R.T.}$ and higher thermal annealing at $T_{\text{a2}} = 900^\circ\text{C}$ produced p-type layers of good quality with maximum hole mobility of $454.5 \text{ cm}^2/\text{Vsec}$ at about 65K.
- J-III.3** 14:45-15:00 **ION BEAM SYNTHESIS OF METALLIC NANOCCLUSERS IN SiO₂: PREDICTIVE COMPUTER SIMULATION VERSUS EXPERIMENTS**, M. Strobel, K.-H. Heinig and W. Möller, Research Center Rossendorf, P.O.Box 510119, 01314 Dresden, Germany; A. Meldrum, C.W. White, and R.A. Zuhr, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA
A kinetic 3D lattice Monte-Carlo (KLMC) method is used to describe nucleation and growth of nanoclusters (NCs) from a space- and time-dependent supersaturated solid solution formed by high-dose ion implantation. Within the framework of homogeneous nucleation, the dependence of the depth- and size-dependent NC distribution on implantation temperature T_{imp} and ion current j is shown. Size and depth distributions of gold NCs in SiO₂ observed after implantation on at different T_{imp} are consistent with the simulation results. The KLMC simulations predict that a controlled variation of the implantation conditions (decreasing T_{imp} or increasing j) can initiate a second nucleation regime, thus leading to a double-peaked size distribution. Corresponding Au⁺ implantations in SiO₂ are discussed with respect to these predictions. Additionally, for the first time the formerly observed shift of Ag implanted into fused silica has been successfully modeled by the introduction of a drift term in the KLMC method. Electrical charging and/or stress as possible driving forces of the Ag drift towards the surface are discussed.

J-III.4 15:00-15:15

OPTICAL PROPERTIES OF INTERACTING Si NANOCCLUSERS IN SiO₂ FABRICATED BY ION IMPLANTATION AND ANNEALING, T. Shimizu-Iwayama, Aichi University of Education, Igaya-cho, Kariya-shi, Aichi 448-8542, Japan and D.E. Hole, P.D. Townsend, University of Sussex, Brighton BN1 9QH, UK

A novel method for the fabrication of luminescent Si nanoclusters in an amorphous SiO₂ matrix by ion implantation is reported. We have studied the effect of dose (excess Si concentration) and annealing condition on the photoluminescence of Si nanoclusters in SiO₂ layers at room temperature. The samples were fabricated by Si ion implantation into SiO₂ on Si wafer and subsequent annealing at 1050°C. After annealing, a photoluminescence band peaked below 1.7 eV has been observed. The peak energy of the photoluminescence is found to be independent of annealing time, while the intensity of the luminescence increases as the annealing time increases. Moreover, we found that the peak energy of the luminescence is strongly affected by dose of implanted Si ions especially in the high dose range (high excess Si concentration). These results indicate that the photons are absorbed by Si nanoclusters, for which the band-gap energy is modified by the quantum confinement effects, and the emission is not simply due to electron-hole recombination inside Si nanoclusters, but is related to defect sites at the interface between Si nanoclusters and SiO₂, for which the energy state is affected by Si cluster-cluster interactions. It seems that nanoclusters react via a thin oxide interface and the local concentrations of nanoclusters play an important role in the peak energy of the photoluminescence

15:15-15:45

BREAK

SESSION IV - Ion Implantation for Optical Applications, Part 2

Chairpersons : H. Atwater, California Institute of Technology, TJ Watson Lab. of Applied Physics, Pasadena, CA, USA

S. Mantl, ISI-IT, Forschungszentrum Jülich, Jülich, Germany

J-IV.1 15:45-16:00

HOMOGENEOUSLY SIZE DISTRIBUTED Ge NANOCCLUSERS EMBEDDED IN SiO₂ LAYERS PRODUCED BY ION BEAM SYNTHESIS, A. Markwitz, L. Rebohle and W. Skorupa, Forschungszentrum Rossendorf Institut für Ionenstrahlphysik und Materialforschung, P.O. Box 510119, 01314 Dresden, Germany
500 nm SiO₂ layers were implanted with 450 keV ($F = 3 \times 10^{16} \text{cm}^{-2}$) and 230 keV ($F = 1.8 \times 10^{16} \text{cm}^{-2}$) Ge ions one after the other in order to produce a nearly homogeneously Ge concentration of about 4 at.% in the insulating layer. During implantation, the substrate temperature was kept close to room temperature. Subsequently, the specimens were annealed between 500°C and 1200°C for 30min. in dry N₂ atmosphere. Cross sectional high-resolution TEM analysis reveals homogeneously distributed Ge nanoclusters (typical size 3 nm) arranged in a broad band in the SiO₂ layer. However, the region close to the surface of the specimens remains always cluster-free independent on the annealing process, where as a narrow Ge nanocluster band at the SiO₂/Si interface is observed at high annealing temperatures. Furthermore, atomic Ge redistribution due to annealing was investigated additionally with an energy dispersive X-ray system equipped at the scanning TEM and RBS.

J-IV.2 16:00-16:15

ION BEAM SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ZnS NANOCRYSTALS IN SiO₂, C. Bonafos, B. Garrido, M. Lopez, A. Romano-Rodriguez, O. Gonzalez-Varona, A. Perez-Rodriguez and J.R. Morante, Departament d'Electronica, Universitat de Barcelona, Diagonal 645-647, 08028 Barcelona, Spain; R. Rodriguez, Asociacion de la Industria Navarra (AIN), 31191 Cordovilla, Pamplona, Spain
II-VI nanocrystalline structures are of particular interest for opto-electronics applications such as sharp-cut filters in the visible and UV regions or electroluminescent and photoluminescent devices. We report here the ion beam synthesis and the structural characterization of ZnS nanocrystals in SiO₂. Electron diffraction and X-Ray diffraction measurements conclude to the precipitation of ZnS nanocrystals having a wurtzite-2H structure and Infra-Red spectroscopy confirms the presence of Zn-S bonding. When increasing the annealing temperature, Transmission Electron Microscopy observations show the Ostwald ripening of the precipitate's coupled with a self-organization in two layers parallel to the free surface. This self-organization has been also detected by Secondary Ion Mass Spectroscopy and its origin is discussed in terms of pure Ostwald ripening process and/or consequence of the implantation damage. First results of the optical analysis of samples co-implanted with Mn at different concentrations are also presented showing the effective doping of the ZnS nanocrystals.

J-IV.3 16:15-16:30

ION BEAM ASSISTED DEPOSITION OF ZIRCONIUM NITRIDES FOR MODULATED OPTICAL INDEX STRUCTURES, L. Pichon, A. Straboni, T. Girardeau, M. Drouet, F. Lignou, Laboratoire de Metallurgie Physique, Université de Poitiers, SP2MI, UMR 6630 CNRS, BP 179, 86960 Futuroscope cedex, France and J. Perrière, Groupe de Physique des Solides, Université Paris VI, tour 23. 2 place Jussieu, 75251 Paris Cedex 05, France

Composition gradients in thin films show interesting mechanical and optical surface applications. Therefore, we focus our study on the zirconium nitrides which show remarkable properties in both aspects. Indeed, the zirconium nitride show optical and electrical properties that depend on the nitrogen content and this material exhibits a transition from metallic ZrN (optical index: $N = 0.5 - i.3.2$) to transparent insulator Zr₃N₄ ($N = 3.2 - i.0.2$). These values lead to an optimum contrast for further optical and electrical characterization. This work deals with the controlled elaboration of homogeneous ZrN and Zr₃N₄ coatings. These have been prepared using reactive dual Ion Beam Assisted Deposition (IBAD) with a Zr target and N₂ reactive gas. We studied the influence of the energy E of the reactive beam on the composition of the nitrides. High energy (> 200 eV) leads to the Zr₃N₄ compound while low energy (~50 eV) gives ZrN. Zr₃N₄ is a metastable phase; so we have studied its decomposition into stable ZrN under high energy ion irradiation (Ar⁺⁺ 340 KeV). This allows the fabrication of both lateral and in depth optical index modulation.

SYMPOSIUM J

J-IV.4 16:30-16:45

ION BEAM AND PHOTOLUMINESCENCE STUDIES OF Er AND O IMPLANTED GaN, E. Alves, M.F. da Silva, J.C. Soares*, R. Vianden**, J. Bartels**, A.Kozanecki***, Instituto Tecnológico e Nuclear (ITN), EN 10, 2685 Sacavém, Portugal; *Centro de Física Nuclear da Univ. de Lisboa, Av. Prof. Gama Pinto 2, 1699 Lisboa, Portugal; **ISKP, Univ. Bonn, Nussallee Str, 53115 Bonn, Germany; ***Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

The annealing behavior and the lattice site location of Er and Er+O implanted into GaN single crystalline epilayers were studied with the RBS/channeling and photoluminescence techniques. After implantation the results show that for doses of $5 \times 10^{14} \text{Er}^+/\text{cm}^2$ the Er ions occupy substitutional sites in the GaN lattice as revealed by detailed angular scans along the $\langle 1011 \rangle$ and $\langle 0001 \rangle$ axes. An increase of the dose to $5 \times 10^{15} \text{Er}^+/\text{cm}^2$ produces a continuous amorphous layer. The damage produced by the implantation starts to anneal at 600°C. For the samples implanted with the lower dose the recovery is almost complete after one hour annealing at 900°C. During the annealing process Er remains in substitutional sites. The presence of O seems to slightly increase the substitutional fraction. Further the photoluminescence signal is more intense for the sample co-doped with oxygen.

J-IV.5 16:45-17:00

THIN AMORPHOUS GALLIUM NITRIDE FILMS BY ION IMPLANTATION, S.R.P. Silva, S.A. Almeida and B.J. Sealy, School of Electronic Engineering, Information Technology and Mathematics, University of Surrey, Guildford, Surrey GU2 5XH, UK

Ion implantation and plasma enhanced chemical vapour deposition have been used to synthesise amorphous gallium nitride (a-GaN) thin films by implanting Ga^+ into amorphous silicon nitride (a-SiN_x) substrates. This route enables the synthesis of large area a-GaN substrates for use as seed layers for growth of crystalline GaN as well as an amorphous semiconductor in its own right. A study of an entire range of a-SiN_x with different compositions 'x' [1] has enabled the choice of the most feasible type of target substrate. It has been shown that nitrogen rich a-SiN_x has a high stress as well as a steady incorporation of N (even with increasing NH₃ entering in the reaction chamber during deposition) which is most likely to break on Ga implantation. X-ray Photoelectron Spectroscopy and Rutherford Backscattering Spectroscopy studies yield information on the chemistry and elemental depth profiles of the material synthesised. Low temperature annealing, compatible with large area glass substrates is then used to increase the thickness of the a-GaN and transform more of the a-SiN_x.

[1] S. A. Almeida and S. R. P. Silva, Thin Solid Films **311**, 133, (1998).

SESSION V - Equipment

Chairperson : B. Svensson, Dept of Electronics, Royal Institute of Technology, Kista-Stockholm, Sweden

J-V.1 17:00-17:30 - Invited -

CHALLENGES AND EQUIPMENT IMPLICATIONS IN ION IMPLANTATION FOR SUB-0.25μm TECHNOLOGY, **K. Funk** and Y. Erokhin, Semiconductor Equipment Operations, Eaton Corporation, Kirchheim, Germany

Scaling down design rules for leading edge CMOS devices to sub-0.25μm forces device manufacturers into ultra low energy implantation as well as into high energy implantation. As a consequence implant equipment manufacturers broaden the spectrum of classical implanter tool set and provide more application dedicated implanter designs. Transition to 300mm can be dealt separately from the transition to the next technology node.

The most challenging process is formation of highly doped sub-100nm p+/n S/D junctions. Fundamental reasons complicating formation of ultra-shallow junctions are due to transient enhanced diffusion (TED) during post implant heat treatment, channeling of low energy implanted Boron, reduced electrical activation of dopant at low thermal budget anneals and enhanced Boron segregation into the native surface oxide. Furthermore close existence of the junctions space charge region and implant defects can cause higher leakage current. Consequently far more aggressive reduction of boron implant energy is required compared to earlier predictions. Radical changes in beamline design have to be done to overcome beam current limitation. Strategies and its limitations will be discussed. Alternative CMOS device architectures are briefly reviewed that can relax S/D junction depth requirements without compromising electrical characteristics of MOS transistors.

Adoption of retrograde wells in mainstream CMOS device architectures formed by high energy implantation will be reviewed as well as triple well device structures and the use of buried layers. Possible epi replacement strategies will be discussed considering its impact on latch-up susceptibility and gate oxide integrity. Other high energy implantation specific aspects like photoresist mask integrity and the use of resist stabilization technology will be mentioned as well as machine related phenomena including differential channeling.

High tilt implantation will dominate medium current implantation. Energy purity, variation of beam divergence and beam incidence angle across the wafers are major process parameters and have to be carefully monitored to enhance Vt- control and to reduce its sensitivity from variations in other channel and well implants.

Wednesday, June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION VI - Ceramics and Oxides

Chairperson : R. Yankow, Forschungszentrum Rossendorf, Dresden, Germany

- J-VI.1** 14:00-14:30 - Invited - **ION IMPLANTATION IN TiO₂: DAMAGE PRODUCTION AND RECOVERY, LATTICE SITE LOCATION AND ELECTRICAL CONDUCTIVITY, R. Fromknecht, I. Khubeis*, S. Massing, O Meyer, Forschungszentrum Karlsruhe, INF, POB 3640, 76021 Karlsruhe, Germany, *Univ. of Amman, Dept. of Physics, Jordan**
Ions with different oxidation states were implanted in TiO₂ (rutile). The lattice disorder as well as the lattice site location of the implanted ions were determined using Rutherford backscattering and channeling (RBS- C) spectrometry. The production of disorder as a function of dose and temperature, and its recovery was studied in detail. Important results are the observation of dynamic recovery at 193 K and above, and thermal recovery in three stages below 293 K in both sublattices. The recovery at 77 K is proportional to $\ln t$, indicating that the activation energy increases with decreasing disorder density. The results concerning the lattice site location of 14 ion species reveal that 13 ions occupy Ti lattice site. With increasing net charge, the maximum soluble concentration decreases by the formation of impurity-defect structure complexes enforced by charge compensation. Directed displacements from the lattice site provide some hints on the structures of these complexes. The electrical conductivity of the implanted samples increased by orders of magnitude as well by defects and by doping. From the temperature dependence it is concluded that the carrier transport occurs by variable-range hopping between localized states. From the dose and temperature dependence of the electrical conductivity especially from its different behaviour for noble gas ions and other ion species it is concluded, that the carrier transport of doped samples occurs by hopping in an impurity band. The hopping process does not seem to depend strongly on the oxidation state and on the electron charge distribution of the implanted ions.
- J-VI.2** 14:30-14:45 **STRUCTURAL STABILITY OF ION BOMBARDED CERAMICS, P.M. Ossi, R. Pastorelli, INFN-Dipartimento di Ingegneria Nucleare, Politecnico di Milano, via Ponzio 34/3, 20133 Milano, Italy**
The nucleation of a crystalline, or of an amorphous phase in binary ceramics ion bombarded under suitable conditions to form dense collision cascades, depends both on non equilibrium and on thermodynamic mechanisms active during relaxation to equilibrium of highly excited matter drops. The Segregation Charge Transfer (SCT) model, already applied with success to many binary alloys, is extended and adapted to interpret structural evolution in ceramics. At the cascade-matrix interface, relaxation to (meta)stable equilibrium is simulated by a Charge Transfer Reaction (CTR) involving a couple of dissimilar atoms: as a result a couple of ionized atoms is formed. We compare the volume of the CTR products to the volume they occupy in the starting compound. The absolute value of the relative volume change induced by a CTR is evaluated and related to the local lattice deformation induced by the same CTR. A threshold volume variation is found, which is associated to the destabilization of the starting compound lattice: volume changes lie above such a threshold in amorphized compounds and below it in crystallized compounds.
- J-VI.3** 14:45-15:00 **EFFECT OF H⁺ AND O⁺ IMPLANTATION ON ELECTRICAL PROPERTIES OF SrBi₂Ta₂O₉ FERROELECTRIC THIN FILMS, Jianming Zeng*, Chenglu Lin*, Lirong Zheng*, A. Pignolet**, M. Alexe**, E. Richter*** and D. Hesse**, *State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, 200050 Shanghai, China; **Max-Planck-Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany; ***Institute of Ion Beam Physics and Materials Research, 01314 Dresden, Germany**
Integration of ferroelectric thin films with the current semiconductor technologies opens a variety of possibilities to improve existing devices or to design new devices. However, up to now, few attempts have been made to implement ion implantation technology into ferroelectric thin films and devices. In this paper, the effect on the crystalline structure and ferroelectric properties of ion implantation in SrBi₂Ta₂O₉ (SBT) ferroelectric thin films has been investigated. 25KeV H⁺, 140KeV O⁺ with doses from $1 \times 10^{14}/\text{cm}^2$ to $3 \times 10^{15}/\text{cm}^2$ were implanted into the Sol-Gel prepared SBT ferroelectric thin films. The X-ray diffraction patterns of SBT films show that no difference appears in the crystalline structure of as-H⁺-implanted SBT films compared with as-grown films, H⁺ and O⁺ co-implanted SBT films show a obvious degradation of crystalline structure. Ferroelectric properties measurements indicate that both remnant polarization and coercive electric field of H⁺ implanted SBT films decrease with increasing the implantation dose. The disappearance of ferroelectricity in H⁺, O⁺ co-implanted SBT films was found. A effective recovery method for the degraded SBT films was studied. The possible mechanism of the degradation in implanted SBT films and the prevention effect of oxygen on the degradation were also proposed.
- J-VI.4** 15:00-15:15 **ANNEALING BEHAVIOR OF DEFECTS IN HELIUM IMPLANTED MgO, H. Schut, A. van Veen, F. Labohm, and A.V. Fedorov, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, E.A.C. Neeft and R.J.M. Konings, ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands**
Virgin MgO (100) single crystals have been implanted with 30 keV ³He⁺ ions to a dose of $5 \times 10^{15} \text{cm}^{-2}$. After implantation the samples have been annealed under air for 30 minutes in a tube oven. The anneal temperature was varied from 575 K to 1375 K in steps of 200 K. The annealing behavior of the defects and ³He has been monitored by three experimental techniques: positron beam Doppler broadening, neutron depth profiling (NDP) and optical absorption in the UV to near-IR region. Compared to the virgin sample, the positron data revealed the presence of near surface implantation defects as a decrease in the defect parameter. The value of this parameter remained unchanged up to 575 K. At 775 K an increase is observed which points at the formation of larger defects. At the same temperatures the NDP data showed no loss or movement of He, contrary to results obtained for a similarly treated spinel (MgAl₂O₄) sample. The observations in MgO lead to the conclusion that below 575 K the vacancy like defects are stabilised by the implanted He atoms. Above this temperature He may dissociate from these small defects, allowing the formation of larger vacancy clusters at which the He becomes trapped again. This annealing behavior is similar to that observed in H and He irradiated Si.

SYMPOSIUM J

15:15-15:30

BREAK

SESSION VII - Poster Session I

Chairpersons : **B. Svensson**, Dept of Electronics, Royal Institute of Technology, Kista-Stockholm, Sweden
J. Lindner, Universität Augsburg, Institut für Physik, Augsburg, Germany

15:30-17:00

See programme of this poster session p. J-16 to J-21.

SESSION VIII - Poster Session II

Chairpersons : **J. Lindner**, Universität Augsburg, Institut für Physik, Augsburg, Germany
B. Svensson, Dept of Electronics, Royal Institute of Technology, Kista-Stockholm, Sweden

17:00-18:30

See programme of this poster session p. J-22 to J-27.

Thursday, June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION IX - New Measurement Techniques

Chairpersons : B. Stritzker, Universität Augsburg, Institut für Physik, Augsburg, Germany

T. Shimizu-Iwayama, Aichi University of Education, Aichi, Japan

- J-IX.1** 9:00-9:30 - Invited - **GLANCING INCIDENCE DIFFUSE X-RAY SCATTERING STUDIES OF IMPLANTATION DAMAGE IN Si, K. Nordlund**, Accelerator Laboratory, P.O. Box 43, 00014 University of Helsinki, Finland; P. Partyka, I.K. Robinson and R.S. Averbach, Materials Research Laboratory, University of Illinois, Urbana, IL 61801, USA; P. Ehrhart, Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, Germany
Diffuse X-ray scattering (DXS) at glancing incidence is a potentially powerful means for elucidating damage structures in irradiated solids. Fundamental to the analysis of diffuse X-ray scattering data is a knowledge of the atomic displacement field around defects, which for implantation damage in crystals like Si has been difficult to obtain using analytical solutions of elastic continuum theory. We present a method for predicting the diffuse scattering pattern by calculating the displacement field around a defect using fully atomistic simulations and performing discrete sums for the scattering intensity. We apply the method to analyze our experimental DXS results of defects produced by 5 keV He and 20 keV Ga irradiations of Si at temperatures of 100 - 300 K. The results show that the Si self-interstitial becomes mobile around 150 K, and that amorphization of silicon by low- and medium-heavy projectiles occurs homogeneously through the buildup of interstitial clusters, and not within single cascade events.
- J-IX.2** 9:30-9:45 **IMAGING OF IMPLANTATION DEFECTS BY X-RAY TOPOGRAPHY COMBINED WITH SURFACE ACOUSTIC WAVE EXCITATION, E. Zolotoyabko**, Technion-Israel Institute of Technology, Haifa 32000, Israel
A novel technique for materials characterization - X-ray topography under high-frequency surface acoustic wave (SAW) excitation - is discussed with a focus on the post-implantation defects imaging. In this method, plane SAWs with a wavelength of 10 μm are introduced into the crystal, creating periodic long-range variations of elastic strain. X-ray topographs from nearly perfect crystals, having such artificially modulated atomic structure, contain alternating bright and dark lines, passing like a ruler through the whole crystal area. Crossing crystal regions with defect-induced atomic disorder, the ruler is getting slightly bent, providing clear defect images, which are not visible without SAW. Thus, an idea is to take diffraction images not from very weak defect-induced static deformation field, but from much more stronger and regular dynamic deformation field created by SAW. Contrast variation is caused by the wave front distortions due to the SAW scattering on the extended defects.
These general considerations are illustrated by X-ray synchrotron topographs taken in situ from LiNbO_3 -based SAW devices with He-implanted waveguide layers. Measurements were performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) in the stroboscopic mode, i.e. synchronizing the electron bunch frequency with the resonant frequency (about 300 MHz) of the SAW device. X-ray diffraction images showed plane SAW propagation through the LiNbO_3 crystals as well as wave front distortions, revealing otherwise invisible screw dislocations and sub-micron He-bubbles, located 300-400 μm from each other.
- J-IX.3** 9:45-10:00 **SYNCHROTRON RADIATION GRAZING INCIDENCE X-RAY DIFFRACTION: A NEW TOOL FOR STRUCTURAL INVESTIGATIONS OF ION IMPLANTED GLASSES, F. Zontone**, ESRF, BP 220, 38043 Grenoble Cedex, France and F. D'Acapito, CNR, Div. Sincr. Trieste e Grenoble, P.le Aldo Moro 7, 00185 Roma, Italy
The availability of very intense and highly collimated synchrotron radiation beams coupled with the grazing incidence geometry makes possible to study ion implanted glasses with X-ray diffraction. We have succeeded, for the first time, to maximize the contribution to the scattering of the metal-rich (clusters) layer by working at the critical angle for total external reflection at the implanted layer-substrate interface. By using the refracted beam as a probe the diffraction profile of the metallic clusters in very diluted samples (a single implant in the 10^{16} at/cm² range) can be extracted by a simple subtraction procedure.
We report some results on SiO_2 glasses implanted with Cu, Ni and Ag ions. The experiments were performed at the ID09 beamline at the ESRF. The samples were illuminated with a $10(\text{h.}) \times 24(\text{v.}) \mu\text{m}^2$ very intense monochromatic beam in the grazing incidence geometry with grazing angles ranging from 0.05 to 0.2 degree. The data were collected by using an imaging plate system in the q range $0.1\text{-}8.5 \text{ \AA}^{-1}$ with integration times in the minute time scale. The 2-D data were integrated in order to obtain the 2 θ intensity profiles previous to the subtraction procedure. The radial integration brings a drastic reduction of the statistical noise and difference profiles can be extracted showing several diffraction peaks resolved enough to enable crystalline phases identification, to retrieve lattice parameters and in some cases to determine clusters sizes. In particular, the accuracy in the lattice parameter determination is shown to be a factor of three better than in EXAFS.
- J-IX.4** 10:00-10:15 **MAGNETIC BEHAVIOR OF Ni^+ IMPLANTED SILICA, O. Cintora Gonzalez**, C. Estournès, J. Guille, IPCMS-GMI (UMR 75040 CNRS), 23 rue du Loess, 67037 Strasbourg Cedex 2, France, D. Muller and J.-J. Grob, Laboratoire Phase (UPR 292 CNRS), 23 rue du Loess, 67037 Strasbourg Cedex 2, France
Two kinds of silica substrates (vitreous silica and silica layers grown on silicon under dry oxygen) were implanted with 30 keV and 160 keV Ni^+ ions to different doses (10^{16} and 10^{17} at/cm²). Depth profiles of nickel were determined by RBS. The magnetic behavior of the implanted silica was investigated at room temperature and at 4 K, using a SQUID magnetometer. The analysis of the magnetization versus applied field curves was performed considering that nickel is present in the samples partly in the form of metal particles, partly as Ni^{2+} ions. The metallic part exhibits a super paramagnetic behavior at room temperature and a ferromagnetic behavior at 4 K whereas Ni^{2+} ions bring a paramagnetic contribution which is appreciable only at 4K. The mean size and the distribution width of the metal particles are estimated from the room temperature curves. The mean size varies from 2 nm to 6.5 nm depending on incident energy and implanted concentration. Increasing incident energy or decreasing implanted concentration make the amount of metallic nickel increase. Whereas the mean particle size increases with decreasing energy and concentration. Finally, no appreciable difference was observed between the two kinds of substrates.

10:15-10:45

BREAK

SESSION X - Group III-V and Other Semiconductors

Chairpersons : T. Shimizu-Iwayama, Aichi University of Education, Aichi, Japan

B. Stritzker, Universität Augsburg, Institut für Physik, Augsburg, Germany

- J-X.1** 10:45-11:15 - Invited - **ATOMIC-LEVEL CHARACTERISATION OF THE STRUCTURE OF AMORPHISED GaAs UTILISING EXTENDED X-RAY ABSORPTION FINE STRUCTURE MEASUREMENTS**, M.C. Ridgway and C.J. Glover, Department of Electronic Materials Engineering, Australian National University, Canberra, Australia, G.J. Foran, Australian Nuclear Science and Technology Organisation, Menai, Australia and K.M. Yu, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, USA
- The structural parameters of amorphised GaAs have been determined from extended x-ray absorption fine structure (EXAFS) measurements. A novel preparation methodology utilising selective chemical etching has been developed to produce artefact-free samples appropriate for transmission EXAFS analysis. In the amorphous phase, a reduction in the coordination number to ~3.85 atoms, relative to the crystalline value of four, was measured about both Ga and As atoms. In addition, the nearest-neighbor bond length and Debye-Waller factor both increased relative to crystalline material. The experimentally-determined structural parameters, including the density of the amorphous phase, were in excellent agreement with theoretical predictions and independent of implant conditions. As a consequence, these values were thus considered representative of intrinsic, amorphous GaAs. Furthermore, it has been proposed that the commonly-observed defective recrystallisation of amorphised GaAs is the result of the incorporation of such intrinsic disorder, including under- and over-coordinated atoms and like-atom bonding, during thermal annealing.
- J-X.2** 11:15-11:45 - Invited - **COMPARATIVE STUDY OF DAMAGE PRODUCTION IN ION IMPLANTED III-V COMPOUNDS AT TEMPERATURES FROM 20K TO 450K**, E. Wendler, B. Breger, W. Wesch, Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany
- The damage evolution at temperatures from 20K to 295K is investigated using a target chamber equipped with cooling system and goniometer, which is connected with a 400kV-implanter and a 3M-Tandetron. Thus, the ion-beam induced damage can be immediately measured by RBS at the corresponding implantation temperature. During implantation at temperatures below 100K the primarily produced defects are stable. Direct impact amorphization and growing of amorphous nuclei by subsequent ions result in the formation of an amorphous layer at 0.2..0.4dpa depending on the substrate material. For temperatures above 295K the ion fluence necessary for amorphization, N_{am}^1 , increases considerably with the implantation temperature T_i , which can be explained assuming a thermally enhanced annealing within the primary collision cascades. For $N_{am}^1 \rightarrow \infty$ this yields a critical temperature T_c . At $T_i = T_c$ the primarily produced clusters dissolve completely and point defect complexes nucleate, resulting in a broad plateau of the defect density versus N_i at a level of about 15%. Thus an equilibrium between defect production, recombination and annealing occurs. Only at very large T_i this equilibrium is interrupted and an amorphous layer forms. For a given material T_c increases slightly with increasing primary nuclear energy deposition per ion and unit depth. T_c corresponds to the reverse temperature of IBIEC and to annealing stages of defects in the corresponding materials. For example, in GaAs and InP the range of T_c agrees with an annealing stage which might be related to the mobility of Ga and P interstitials, respectively.
- J-X.3** 11:45-12:00 **SHALLOW JUNCTIONS IN p-In₅₃Ga₄₇As BY ION IMPLANTATION**, M.N. Blanco, E. Redondo, C. Leon, J. Santamaria, G. Gonzalez-Diaz, Dpto. Electronica, Fac. CC. Fisicas, U. Complutense, 28040 Madrid, Spain
- Ion implantation is a well known method to make shallow and abrupt junctions for semiconductor devices, but a good characterization of the possible defect traps linked to the implantation process is needed. In this communication, a detailed study (I-V, C-V, C-f) is conducted to look at the influence of trap levels and recombination centers on the conduction mechanism of p-n⁺ junctions made by a 50 keV Si implantation into Zn doped In₅₃Ga₄₇As/InP.
- The I-V characteristics at variable temperature indicate that the dominant conduction mechanism at forward bias is recombination in the space-charge zone, with ideality factors of 1.5 at 300K and an activation energy of 0.51 eV. The reverse characteristics show that the conduction process is described by a thermally-activated trap-assisted tunneling mechanism at low bias (0.25 eV), and by trap-assisted tunneling at high bias. A deep level at 0.36 eV is observed by admittance spectroscopy measurements using the Kramers-Kronig transforms, with an estimated concentration of 0.02% of the net shallow acceptor concentration, and its origin can be probably ascribed to the Zn acceptor present in p-InGaAs.
- J-X.4** 12:00-12:15 **EFFECTS OF HYDROGEN IMPLANTATION INTO GaN**, S.J. Pearton, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA; R.A. Wilson, Consultant, Winnetka, CA 92065, USA; J.M. Zavada, US Army Research Office, RTP, NC 27709, USA; C.Y. Song, M.G. Weinstein and M. Stavola, Department of Physics, Lehigh University, Bethlehem PA 18015, USA
- Proton implantation in GaN is found to reduce the free carrier density through two mechanisms - first, by creating electron and hole traps at around $E_c - 0.8$ eV and $E_v + 0.9$ eV that lead to compensation in both n- and p-type material, and second, by leading to formation of (AH)⁰ complexes, where A is any acceptor (Mg, Ca, Zn, Be, Cd). The former mechanism is useful on creating high resistivity regions for device isolation, whereas the latter produces unintentional acceptor passivation that is detrimental to device performance. The strong affinity of hydrogen for acceptors leads to markedly different redistribution behavior for implanted H⁺ in n- and p-GaN due to the chemical reaction to form neutral complexes in the latter. The acceptors may be reactivated by simple annealing at ≥600°C, or by electron injection at 25-150°C that produces debonding of the (AH)⁰ centers. Implanted hydrogen is also strongly attracted to regions of strain in heterostructure samples during annealing, leading to pile-up at epi-epi and epi-substrate interfaces. IR spectroscopy shows that implanted hydrogen also decorates V_{Ga} defects in undoped and n-GaN.

SYMPOSIUM J

J-X.5 12:15-12:30

PHOTOLUMINESCENCE STUDIES OF NEUTRON TRANSMUTATION DOPED InP:Fe, B. Mari, M.A. Hernandez, F.J. Navarro, Dep. Fisica Aplicada, Universitat Politecnica de Valencia, Cami de Vera s/n, 46071 Valencia, Spain and R. Fornari, CNR-MASPEC Institute, Via Chiavari 18/A, 43100 Parma, Italy

Neutron-irradiated InP:Fe semi-insulating crystals have been investigated by photoluminescence (PL). Samples were irradiated with thermal neutrons at different fluences yielding concentrations for Sn-transmuted atoms between 10^{15} and $4 \cdot 10^{16} \text{ cm}^{-3}$. The photoluminescence spectra of all irradiated samples exhibited two peaks related to band to band (P_{BB} , 1.417 eV) and donor-acceptor (P_{DA} , 1.378 eV) transitions. The intensity of these peaks decreases for increasing irradiation doses, due to the generation of nonradiative recombination centres associated to irradiation. The thermal annealing changes the relative concentration of the irradiation-related defects and their evolution is followed by the PL spectra. The intensities of the P_{BB} and P_{DA} peaks are accordingly recovered as the temperature is increased. Furthermore two new bands appear clearly: the first one is located at 1.35 eV, it becomes visible after annealing at 350°C and disappears for annealing at 650°C; the second one is located at 1.395 eV and appears in the spectra of samples annealed at 450°C. The relative intensities of PL peaks were seen to change with the excitation laser power. This experimental fact provided additional information about defect concentrations and transition probabilities. The 1.35 and 1.378 eV were found to shift their position for increasing laser excitation. This blue shift suggests that these bands are related to donor-acceptor pair transitions. The possible nature of these defects will be discussed.

12:30-14:00

LUNCH

Thursday, June 18, 1998

Jeudi 18 Juin 1998

Afternoon

Après-midi

SESSION XI - New Phase Formation, Part 1

Chairpersons : K. Nordlund, Accelerator Laboratory, University of Helsinki, Finland

C. Lin, Shanghai Inst. of Metallurgy, Chinese Academy of Sciences, Shanghai, China

- J-XI.1** 14:00-14:30 - Invited - **NANOCRYSTAL FORMATION IN SiO₂: EXPERIMENTS, MODELING AND COMPUTER SIMULATIONS**, **K.-H. Heinig**, B. Schmidt, A. Markwitz, R. Grötzschel, M. Strobel, J. von Borany, Research Center Rossendorf, PO Box 510119, 01314 Dresden, Germany
The ion beam synthesis of nanoclusters in SiO₂ is becoming an expanding field of interest due to potential applications. For instance, nonvolatile random access memories can be based on charging of silicon nanocrystals within the gate oxide of MOS transistors, and the electro-luminescence of Ge clusters in SiO₂ offers the potential for integration of opto- and microelectronics. The properties of ion beam synthesized nanoclusters depend strongly on implantation and annealing conditions. These conditions control the competition between effects like ion beam mixing, chemical reactions, diffusion and precipitation, which may result even in self-ordering phenomena. A fundamental understanding of these effects facilitates the search for ion beam synthesized nanocluster distributions, which are optimized for specific applications. Here we present comprehensive experimental (RBS, cross-section TEM, ...) and computer simulation (kinetic MC, reaction-diffusion equations) studies of ion beam synthesis of nanocrystals with special attention to Ge⁺ ion implantation into thermally oxidized silicon wafers.
- J-XI.2** 14:30-14:45 **CONTROLLING THE DENSITY DISTRIBUTION OF SiC NANOCRYSTALS FOR THE ION BEAM SYNTHESIS OF BURIED SiC LAYERS IN SILICON**, **J.K.N. Lindner** and B. Stritzker, Universität Augsburg, Institut für Physik, 86135 Augsburg, Germany
High-dose carbon implantation into silicon and subsequent thermal annealing at 1250°C can be used to synthesize buried homogeneous epitaxial SiC layers in Si(111) and Si(100). Both the crystalline structure of the buried layer and the abruptness of interfaces depend on the implantation temperature and ion current density, because these parameters determine the structural starting conditions prior to annealing. We have used RBS/channeling to study the carbon depth distribution and substrate crystallinity as a function of dose after 180 keV C⁺ implantation at temperatures between 400 and 600°C. High-resolution cross-section TEM was applied to monitor the depth distribution of SiC precipitates. It is shown that oriented, nm-sized 3C-SiC precipitates are formed during implantation, the size of which is almost identical, independent of implantation conditions and depth position. The SiC nanoprecipitates are subjected to ballistic destruction. At a slightly temperature dependent threshold carbon concentration, the silicon lattice turns amorphous, accompanied by a significant reduction of the SiC precipitate density. Upon a dose increase, beam induced nucleation of randomly oriented SiC crystals occurs in amorphized regions. The knowledge of these formation mechanisms can be exploited to generate box-like depth distributions of oriented SiC precipitates, which provide optimized starting conditions for the formation of epitaxial 3C-SiC layers in Si during a subsequent anneal.
- J-XI.3** 14:45-15:00 **EFFECT OF OXYGEN ON ION-BEAM INDUCED SYNTHESIS OF BURIED SiC LAYER IN SILICON**, V.V. Artamonov, M.Ya. Valakh, **N.I. Klyui**, V.P. Melnik, A.B. Romanyuk, B.N. Romanyuk, V.A. Yuhimchuk, Institute of Semiconductor Physics, 45 pr. Nauki, 252028 Kiev, Ukraine
The properties of Si-structures with buried silicon carbide (SiC) layers created by high dose carbon implantation into Cz-Si or Fz-Si wafers followed by high-temperature annealing were studied by Raman and infrared (IR) spectroscopy. Effect of additional oxygen implantation on the peculiarities of SiC layer formation was also studied.
It was shown that under the same implantation and post-implantation annealing conditions the buried SiC layers is more effectively formed in Cz-Si or in Si (Cz- or Fz-) subjected to additional oxygen implantation. So, we can conclude that oxygen in silicon promotes the SiC layer formation due to SiO_x precipitate creation and accommodation of the crystal volume in the region where SiC phase is formed. The proposed model was confirmed by results of measurements of strain depth distribution in Si-structures with SiC buried layer. The properties of buried SiC layers after removal of silicon overlayer were also studied. The carbon segregation and amorphous carbon film formation on the SiC grain boundaries were revealed. The mechanisms of the effects observed are discussed.
- J-XI.4** 15:00-15:15 **NON-LOCAL APPROACH TO MODELING OF NANOCUSTER EVOLUTION IN ION-IMPLANTED LAYERS**, **V.A. Borodin**, RRC Kurchatov Institute, 123182 Moscow, Russia; K.-H. Heinig and B. Schmidt, FZ Rossendorf, P.O.Box 510119, 01314 Dresden, Germany
Both implantation and subsequent annealing of ion-implanted layers in semiconductor device materials are often accompanied with implant precipitation. Spatially non-uniform distributions of nanoclusters, implanted impurity and atomic species diffusing from the environment result in complicated and often unexpected effects of implanted atom redistribution. The examples of such effects are self-organization in nanocluster structures due to the non-uniform Ostwald ripening and nanocluster dissolution due to chemical reactions with impurities diffusing from the annealing atmosphere.
In this report we propose a non-local analytical approach that allows to describe the evolution of nanocluster ensembles during ion implantation and post-implantation annealing. Application of this approach to the non-uniform Ostwald ripening provides reasonable explanation of specific features of precipitate band layering predicted by Monte-Carlo simulations. On the other hand, the account of chemical reactions in the developed model provides good quantitative description of the dissolution and phase transformation of Ge clusters in Ge⁺ implanted SiO₂ layers during high- temperature annealing in oxidizing atmosphere.

15:15-15:45

BREAK

SESSION XII - New Phase Formation, Part 2

Chairpersons : C. Lin, Shanghai Inst. of Metallurgy, Chinese Academy of Sciences, Shanghai, China

K. Nordlund, Accelerator Laboratory, University of Helsinki, Finland

J-XII.1 15:45-16:00

STABILISATION AND PHASE TRANSFORMATION OF HEXAGONAL RARE-EARTH SILICIDES ON Si(111), A. Vantomme, M.F. Wu, S. Hogg, U. Wahl, W. Deweerdt, H. Pattyn and G. Langouche, Instituut voor Kern- en Stralingsfysika, K.U. Leuven, 3001 Leuven, Belgium, S. Jin and H. Bender, IMEC, 3001 Leuven, Belgium

Epitaxial, hexagonal rare-earth silicides, such as $\text{ErSi}_{1.7}$, can be formed using channeled ion beam synthesis (CIBS). In the case of Gd-silicide, an orthorhombic GdSi_2 phase exists at high temperature. The transition temperature is related to the thickness and crystalline quality of the silicide. In the case of the lightest rare-earth metals, such as Nd, silicides only exist in a tetragonal or orthorhombic phase, which cannot grow epitaxially on Si(111). However, introduction of a fraction yttrium ($\text{YSi}_{1.7}$ also possesses the aforementioned hexagonal lattice) drives the Nd-Si system into a hexagonal lattice structure. A combined RBS/C, XRD and TEM study shows that an epitaxial, continuous ternary silicide is formed (and not a mixture of binaries) with a hexagonal structure. The lattice parameters of this new metastable phase have been determined using a combination of XRD and channeling. This ternary silicide is stable up to 950°C. Further annealing, however, results in a gradual transformation into polycrystalline phases. The experimental results will be compared to total energy calculations of these (meta-) stable RE-silicides, using the density functional theory (DFT). From a combination of experimental and theoretical results, more information on the lattice parameters and strain-values will be deduced for a tentative hexagonal $\text{NdSi}_{1.7}$ structure, a phase so far unobserved.

J-XII.2 16:00-16:15

MODELLING HIGH-TEMPERATURE CO-IMPLANTATION OF Al^+ AND N^+ IMPLANTATION OF SILICON CARBIDE: THE EFFECTS OF STRESS ON THE IMPLANT AND DAMAGE DISTRIBUTIONS, D.V. Kulikov, Yu.V. Trushin, A.F. Ioffe Physico-Technical Institute of RAS, 26 Polytechnicheskaya str., 19402 St. Petersburg, Russia; R.A. Yankov, U. Kreissig, W. Fukarek, A. Mücklich, W. Skorupa, Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf e.V., PF 510119, 01314 Dresden, Germany; J. Pezoldt, Institut für Festkörperelektronik, TU Ilmenau, PF 100565, 98684 Ilmenau, Germany

This work is an initial attempt to model the fundamental processes that occur when SiC is implanted at elevated substrate temperatures T_i (200°-800°) with high doses of N^+ and Al^+ ions to synthesise buried layers of $(\text{SiC})_{1-x}(\text{AlN})_x$. The theoretical treatment has involved ballistic calculation of the implant and damage profiles by means of computer codes (TRIRS and DYTRIRS) developed for modelling complex, multi-elemental targets. The influence of the mechanical stress induced by implanted ions has been taken into account by adding a special term to the differential equations describing the evolution of the implant and damage distributions. Results from the simulations have been correlated with data obtained by RBS/C, ERDA, PIRR and XTEM. The theoretical approach described has enabled one to determine the activation energies of migration of silicon atoms in the host lattice, and the recombination process of point-defect recombination process in the silicon and carbon sublattices as well as the role of stress on the impurity and defect distributions.

J-XII.3 16:15-16:30

POINT DEFECTS-He AND He-He INTERACTION DURING VOID FORMATION INDUCED BY He IMPLANTATION IN SILICON, V. Raineri, S. Coffa, CNR-IME-TEM, Catania, Italy; M. Saggio, F. Frisina, SGS-Thomson Italy; S.U. Campisano, INFN and Dip. Fisica Catania, Italy

Voids in silicon have a quite large interest both from the fundamental and the application point of view. We recently suggested and deeply investigated gettering and lifetime control by void in silicon. Void application and properties are strongly influenced by the void formation procedure and sample structure. In this work we present a detailed work on void formation in silicon by He implantation. He has been implanted in Cz, Fz and epitaxially grown silicon to establish the importance of substrate impurities on He bubble formation. Moreover, He as been implanted in surface silicon amorphous layers produced by multiple silicon implants. The experiments were performed carefully controlling substrate temperature during He implantation. The He-He interaction has been investigated by multiple He implants at several doses and different energies. He investigated doses are in the $1(10^{16} - 1(10^{17})\text{cm}^{-2}$ range while energies between 20 and 300 keV have been used. He bubble formation and their evolution in void by subsequent thermal processes at temperatures in the 800(1000-°C range has been determined by transmission electron microscopy and high resolution transmission electron microscopy. The data clarify the role of point defect-He and He-He interaction for either bubble formation and their evolution in void and a model describing the process is given. The correlation with device application is also discussed.

J-XII.4 16:30-16:45

STABILITY OF CAVITIES FORMED BY He^+ IMPLANTATION IN SILICON, F. Roqueta, PHASE-CNRS, B.P.20, 23 Rue du Loess, 67037 Strasbourg Cedex 2, France and LMP (Univ. Tours) 16 rue Pierre et Marie Curie, B.P. 7155, 37071 Tours Cedex 2, France; A. Grob, J.J. Grob, J.P. Stoquert, PHASE-CNRS, B.P. 20, 23 Rue du Loess, 67037 Strasbourg Cedex 2, France; R. Jérísian, L. Ventura, LMP (Univ. Tours) 16 rue Pierre et Marie Curie, B.P. 7155, 37071 Tours Cedex 2, France

It is known that microscopic cavities are efficient gettering sites for metallic impurities in silicon. In the present study, they were formed in $\langle 111 \rangle$ silicon by 40 keV room temperature He^+ implantation at doses of 5×10^{16} and 10^{17}cm^{-2} , followed by a thermal treatment under N_2 atmosphere, using either Rapid Thermal Annealing (RTA) or conventional furnace. Both helium desorption and cavities evolution were studied using respectively non-Rutherford (resonant) proton scattering and Rutherford Backscattering-Channeling (RBS-C) analysis and Transmission Electron Microscopy (TEM). The retained fraction of helium is shown to depend on which type of furnace is used (in relation to their respective heating rates), and to decrease with annealing time much slower than the first order gas release model. When calibrated using TEM observations, the RBS-C analysis is shown to be sensitive to the total cavities surface, a quantity which also slowly decreases with annealing duration. A model is proposed to explain the various mechanisms involved in cavity formation and stability.

SYMPOSIUM J

J-XII.5 16:45-17:00

CONTROL OF METALLIC CLUSTER FORMATION IN GLASS BY ION IRRADIATION, E. Valentin*,**H. Bernas** and F. Creuzet***, *Laboratoire CNRS/St. Gobain, 39 quai L. Lefranc, 93303 Aubervilliers, France; **Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, CNRS-IN2P3, Bât. 108, 91405 Orsay, France; ***present address: Corning Research Center, Fontainebleau, France
Annealing of sodocalcic glasses containing $< 10^{-3}$ Cu₂O by weight forms small (5-10 nm) Cu and Cu₂O clusters. Can the cluster nucleation and growth process be controlled via ion irradiation? We used heavy ions ranging from Si to Br at MeV energies and fluences ranging from 10^{13} to 10^{16} ions. cm⁻²; the samples were characterized by optical absorption spectroscopy, standard and high resolution transmission electron microscopy (HRTEM), and by atomic force microscopy (AFM) on the fracture facets of the glass. We find that (i) ion irradiation is species-selective: only (spherical) metallic Cu clusters are formed; (ii) the cluster distribution is restricted to depths corresponding to the ion stopping range; (iii) the Cu cluster distribution as determined by both HRTEM and AFM is narrow, its median size is small and fluence-dependent. These results can be compared to Monte-Carlo simulations of irradiation-induced growth, and extended to other metals.

J-XII.6 17:00-17:15

FABRICATION OF [110]-ALIGNED Si QUANTUM WIRES EMBEDDED IN SiO₂ BY LOW-ENERGY OXYGEN IMPLANTATION, Yukari Ishikawa and N. Shibata, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta, Nagoya 456-8587, Japan; S. Fukatsu, Department of Pure and Applied Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

In this paper, we demonstrate a simple, non-lithographic method for creating Si QWRs embedded in SiO₂ by low energy oxygen implantation on a V-groove patterned substrate.

Separation by implanted oxygen is a technique to form a buried SiO₂ layer in Si. The second isolation of the top Si in lateral directions provides Si/SiO₂ QWRs. Such QWRs have been achieved by optical or electron-beam lithography followed by anisotropic etching. However, process-induced damage and defect trap density at the oxide interface degrade optical or electrical properties of QWRs.

Oxygen ion (25keV-O⁺) implantation was performed at 700°C followed by ex situ annealing at 1280°C for 6 hours in N₂ flood. The cross-section of the V-grooves were checked by transmission electron microscopy. Si QWRs aligned to [110] appeared at the bottom-center of the V-groove at dose value of 2.7×10^{17} /cm². The [110]-cross-section of the Si QWR is a hexagon encompassed by four Si{111} and two Si{001} lateral facets. The formation mechanism is interpreted in terms of oxygen enrichment near the V-groove bottom which arises from geometrical effects in the presence of lateral ion straggling.

J-XII.7 17:30-17:45

WAVE-ORDERED NANOSTRUCTURES FORMED ON SOI WAFERS BY REACTIVE ION BEAMS, V.K. Smirnov, D. S. Kibalov, S.A. Krivelevich, P.A. Lepshin, E.V. Potapov. Institute of Microelectronics RAS, 3 Krasnoborskaya street, 150051 Yaroslavl, Russia; R.A. Yankov, W. Skorupa, Institut für Ionenstrahlphysik und Materialforschung, P.O. Box 510119, 01314 Dresden, Germany; V.V. Makarov, A.B. Danilin, Centre for Analysis of Substances, 1/4 Sretensky Blvd., 103045 Moscow, Russia

Wave ordered structures (WOS) of nanoscale dimensions have been formed using low energy oxygen and nitrogen ion beams. We show that WOS development and wavelength depend on ion beam energy, incidence angle and sample temperature. Nitrogen beam proves to be more suitable for several reasons. First, WOS produced by nitrogen beams are planar. Secondly, they are stable and highly coherent. Third, they have nanometer scale wavelengths (10-200 nm). The geometry and chemical composition of individual waves in WOS arrays formed on SOI (SIMOX) wafers have been studied using SEM, AFM and Auger spectroscopy. SOI WOS structures are promising for the modern microelectronics technology.

17:45-17:50

CLOSING SESSION

END OF SYMPOSIUM J

SYMPOSIUM J
SYMPOSIUM J
POSTER SESSIONS

Wednesday June 17, 1998
Mercredi 17 juin 1998

Afternoon
Après-midi

SESSION VII - Poster Session I
15:30-17:00

- J-VII/P1** RELAXATIONAL SEGREGATION IN ION-BOMBARDED METAL SILICIDES, M.G. Stepanova, Institute of Applied Mathematics RAS, Miusskaya sq. 4, 125047 Moscow, Russia
Recently, a new kind of radiation-induced segregation in ion-bombarded compounds was found theoretically (M.G. Stepanova, Nucl. Instr. Meth. B95(1995)481). The new kind of segregation is related to the relaxation of stresses generated in solids under ion bombardment: ion-induced collision cascades lead to a powerful transfer of the target's material which creates considerable pressure gradients. These give rise to relaxation fluxes proportional to the gradient of the stresses and to the material diffusivity. In a compound material the component's diffusivities are, as a rule, different. Thus, the stresses relax preferentially due to the more mobile component which leads to its depletion in the stressed region, at depths comparable to the mean ion range in the target. In this paper we consider the effect of relaxation-induced segregation in metal silicides. A compilation of experimental data on ion-induced changes of subsurface composition in the silicides is presented; from their comparison with our calculations it is concluded that the new kind of segregation is common to the silicides. It is shown that, due to a higher mobility of silicon, an interlayer enriched in metal arises in the silicides during the ion bombardment. It is concluded that the ion bombardment of major metal silicides leads to a self-organized redistribution of components and formation of nanoscale interlayers enriched in metal at depths comparable to the mean penetration depth of the bombarding ions.
- J-VII/P2** WITHDRAWN
- J-VII/P3** WITHDRAWN
- J-VII/P4** MECHANISM OF ANOMALOUS DIFFUSION OF ION-IMPLANTED PHOSPHORUS IN SILICON, A.R. Chelyadinskii, V.A. Burenkov, Byelorussian State University, Pr. F. Skarina 4, 220050 Minsk, Belarus
Diffusion of ion-implanted phosphorus during rapid thermal annealing and thermal furnace annealing is investigated in silicon and silicon layers previously doped with Ge and C. These impurities are the traps for interstitials Si atoms via the "Watkins substitution". Enhanced diffusion is connected with pair: P atom - Si atom (PI). From our structural investigations it follows that stable interstitial complexes with phosphorus atom do not form. The pair of PI is formed when P and Si atoms insert in the same interstitial site. Atoms of P and Si have not chemical covalent bond; the tie is provided with potential relief of crystal. In the frame of this model observed experimentally regularities are described: dependence of phosphorus diffusion coefficient on duration of annealing, non-dependence of diffusion coefficient on annealing temperature, displacement of the impurity distribution towards the surface during annealing. The diffusion equations involve formation and destruction of the PI and Si-Si pairs, replacement of P atoms from the nodes and capture on vacancies, annihilation of self-interstitials and vacancies. Evolution of the depth distribution of the surplus point defects during annealing is analysed too. The sharply unhomogeneous distribution of the self-interstitials near surface provides with the displacement phosphorus profiles.
- J-VII/P5** DEFECT FORMATION IN SILICON WAFER SURFACE LAYER AND ITS INFLUENCE ON THE BULK PROPERTIES, K.L. Enisherlova, T.F. Rusak, Sc. & R Institute "Pulsar", St. Okružnoi proezd 27, Moscow, Russia, G.K. Ippolitova, T.M. Tkacheva, G.N. Petrov, ELLINA-NT, R & D Co., 38 St. Vavilova, Moscow, Russia
By using the oxygen and carbon ion implantation into silicon wafers grown by floating zone technique as a tool the precipitation process in the presence of carbon is investigated. The defect structure formation and its transformation under high temperature treatment are a function of the presence and interaction between the native point defects and impurities (first of all, oxygen and carbon). The analysis of carbon influence on the precipitation in silicon is reported. It is shown that it is possible to distinguish different kind of defects that formed on the dependence of presence or absence of carbon. The analysis of the implantation conditions and the following annealing conditions on the type and density of created defects is carried. It is shown that oxygen precipitation can appear to be in the presence of carbon at lower residual oxygen concentration than in the absence of carbon. This differences in residual oxygen concentration can reach two orders of magnitude. In the presence of carbon is possible to observe oxygen precipitation even in the silicon samples grown by floating zone technique. It is necessary to control these processes during the whole technological cycle to obtain the desired quality of the silicon wafer bulk.
- J-VII/P6** OSCILLATIONS OF CRITICAL NUCLEUS DURING HIGH-TEMPERATURE ION IMPLANTATION IN CRYSTALLINE LATTICE, G.V. Gadiyak, Institute of Computational Technologies, Russian Academy of Sciences, Siberian Division, Prospekt Lavrentjeva 6, 630090 Novosibirsk, Russia
A simple model for the calculation of a critical nucleus and nucleation rate under high-temperature ion implantation in crystalline lattice for steady-state case has been suggested. This model considers evaporation and sticking reactions of doping atoms with clusters of size i (i is the number of atoms). The rate constants were calculated in diffusion approximation. Oscillations of the size of a critical nucleus as a function of doping concentration was obtained from kinetic model of nucleation. Comparison with classical nucleation theory shows that the principle reason of the oscillations are extremely small magnitudes of sticking rate constants compared to evaporation rate constants and high the concentration of doping atoms in the crystalline lattice. Results of nucleation and cluster growth during HT ion implantation are compared with the process of nucleation in supersaturated gas phase.

- J-VII/P7** THE FORMATION OF COPPER IONS WITH DIFFERENT VALENCE STATES IN CuO UNDER Li⁺-DOPING, IRRADIATION AND PLASTIC DEFORMATION: SOFT X-RAY EMISSION STUDY, D.A. Zatsepin, V.R. Galakhov, B.A. Gishzevski, E.Z. Kurmaev, S.V. Naumov, Institute of Metal Physics, 620219 Ekaterinburg GSP-170, Russia

The influence of Li⁺-doping, irradiation and shear under pressure on the oxygen *p*-band and valence states of copper ions in CuO was studied using soft x-ray spectroscopy. Li⁺-doping as well as the processes of plastic deformation and irradiation with electrons and He⁺ strongly transforms the O_{1s} spectrum shape. In the case of irradiation and shear under pressure the transformation of the spectrum shape is explained by the appearing and growth of Cu₂O-phase content. The doping by lithium leads to the appearance of copper ions with formal valence of 3+. It was also established that the presence of lithium ions prevents Cu₂O-phase forming without any dependence on plastic deformation value (the so-called compensation effect). The reasons and possible mechanisms of the formation of copper ions with dissimilar valence states and phase transitions in the oxides studied are discussed.

- J-VII/P8** WITHDRAWN

- J-VII/P9** FORMATION OF SiO₂ PHASE IN SILICON ENHANCED BY MICROCAVITIES AND POLYVACANCIES, A.A. Efremov, V.G. Litovchenko, Institute of Semiconductor Physics, 45 Propekt Nauki, Kiev 252028, Ukraine

The presentation dedicates to experimental and theoretical results dealing with buried oxide layer formation in the framework of the so called Low-Dose Approach Combined with Optimized Defect Engineering - LDACODE. This approach is based on the use of multiple low dose oxygen ion implantation, intermediate annealing cycles and intermediate ion implantation(s) with special impurities (H₂, C, etc). The introduction of these impurities is used to obtain the appropriate conditions for enhanced growth of the SiO₂ phase at definite depth. In the case of H₂ implantation these conditions are achieved due to the development of an ensemble of nanobubbles and free volume generation for SiO₂ nucleous accommodation. We consider the process using computer simulation taking into account H association and nanobubbles development. The interaction of oxygen with silicon is considered in two aspects: "ordinary" oxidation, accompanied by stressed SiO₂ precipitation growth and Si interstitial injection and an enhanced oxidation of silicon in a local nanobubbles. The main factor resulting in super thin SiO_x seed layer formation observed experimentally proved to be the strain free selective oxidation of silicon in a close vicinity of nanobubbles. However, complex interactions between different types of defects and precipitates are found to be important in this process also.

- J-VII/P10** NON-LINEAR PHASE TRANSFORMATIONS IN SiO₂ FILMS INDUCED BY O₂⁺ ION IMPLANTATION, A.A. Efremov, G.Ph. Romanova, Institute of Semiconductor Physics, 45 Prospekt Nauki, Kiev 252028, Ukraine

The results of SIMS depth profiling of SiO₂ films implanted with the same dose of O⁺ and O₂⁺ ions are presented. In the case of O⁺ implantation a layer with modified structure is located near the external surface of the film. Its location and width correspond to the depth distribution of primary defects generated by ions. In the case of O₂⁺ implantation the modified layer is much more pronounced, very thin (10 nm) and is located at some distance from the surface of the film. The model of the process in the latter case have been developed and respective simulation was carried out. The model includes such points. (i) Just after incoming molecular ion is dissociated. (ii) After this two particles move in correlated manner while electronic energy losses remain dominating and angles of scattering are small. (iii) At some depth nuclear energy transfer increase and the subcascades proved to be overlapped with very high density of defects. Due to this the angles of scattering of moving particles increase also. (iv) As a result correlativity in their trajectories is vanished and abrupt decrease both of the cascade overlapping and density of defects takes place at the rest of their path. (v) As a result of this non-linear and self regulated process a very high density of defects prove to be localized in thin buried layer. (vi) Strongly modified structure is formed after rapid relaxation of this defects without their out-diffusion.

- J-VII/P11** THERMAL STRESS RESISTANCE OF ION IMPLANTED MgO AND SAPPHIRE CRYSTALS, V. Gurarie, D. Jamieson, R. Szymanski, A. Orlov, School of Physics, MARC, University of Melbourne, Melbourne, Australia; J. Williams, M. Conway, Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, ANU, Canberra, Australia

Monocrystals of magnesium oxide and sapphire have been subjected to ion implantation with 86 KeV Si⁺ ions to a dose of 5.0x10¹⁶cm⁻² and with 3 MeV H⁺ ions to a dose of 4.8x10¹⁷cm⁻² prior to thermal stress testing in plasma. Implantation-induced near-surface damage is analysed by ion channeling using 2 MeV He⁺ ions. Implantation with 86 KeV Si⁺ ions is shown to introduce damage in the near-surface structure, which makes crack nucleation easier under the applied stress. At the same time the high-density crack system which is developed considerably reduces the degree of fracture damage. The critical implantation doses which produce a noticeable change in the thermal stress resistance are determined. Ion implantation with 3 MeV H⁺ ions results in the formation of large-scale defects, which produce low density crack system and cause a considerable reduction in the resistance to damage. Possible mechanisms involved in crack nucleation are discussed.

- J-VII/P12** INFLUENCE OF ARGON AND HYDROGEN IONS ENERGY ON THE STRUCTURE OF a-Si:H PREPARED BY ION-BEAM-ASSISTED EVAPORATION, H. Rinnert, M. Vergnat, G. Marchal, Laboratoire de Physique des Matériaux, (U.M.R. au C.N.R.S. No.7556), Université Henri Poincaré Nancy I, B.P. 239, 54506 Vandoeuvre-lès-Nancy Cedex, France; A. Burneau, Laboratoire de Chimie Physique pour l'Environnement, (U.M.R. au C.N.R.S. No.7564), Université Henri Poincaré Nancy I, 405 rue de Vandoeuvre, 54506 Villers-lès-Nancy Cedex, France

Hydrogenated amorphous silicon films were deposited by ion-beam-assisted evaporation onto substrates maintained at 120 °C. The gas introduced in the ECR ion source were pure hydrogen or an argon-hydrogen mixture. The energy of the ions was varied by biasing the substrate. The hydrogen bonding configurations were obtained from infrared transmission measurements and the stability of hydrogen was followed by thermal desorption spectrometry experiments.

The samples prepared with pure hydrogen and without bias contain SiH and SiH₂ bonds. The oxygen-related bands are important. The hydrogen effusion spectrum presents a peak at 400 °C. When the hydrogen ions energy increases from 0 to 300 eV, the hydrogen bonding does not vary but the post-oxidation is suppressed. The effusion spectrum shows another peak at 550 °C. These experiments show that bombardment by light ions accelerated with a moderate voltage can produce a densification of the film structure and an increase of the hydrogen stability.

The samples prepared with an argon-hydrogen mixture present an identical evolution. The presence of argon does not change the concentration and the bonding of hydrogen but the bombardment of the evaporated film by the heavy argon ions is more efficient and the densification is obtained with an energy equal to 20 eV.

- J-VII/P13** ION IMPLANTATION AS A METHOD FOR INCREASING PERFORMANCE OF DIAMOND PHOTODETECTORS, A.G. Zacharov, V.S. Varichenko, HEI&FD Lab., Belarussian State University, 220080 Minsk, Belarus, and A.M. Zaitsev, LGBE, Fern Universität Hagen, 58084 Hagen, Germany

Type Ila natural diamond samples implanted with 20 to 300 keV and 13.6 MeV B⁺ ions at doses within a range of 3x10¹⁴ to 1.25x10¹⁵cm⁻² have been investigated by microwave photoconductivity technique with light excitation at wave lengths from 200 to 800nm. A strong increase of photosensitivity of the irradiated samples has been observed when illuminating the non-irradiated sides. A model of a deep penetration of defects and internal mechanical strains into diamond during ion irradiation has been developed. As a result of this effect a passivation of the recombination centres in diamond bulk occurs increasing its photoconductivity sensitivity. A method for increasing performance of diamond UV photo-detectors is proposed.

- J-VII/P14** ESR OF SILICON IMPLANTED WITH 5.68 GeV Xe IONS, N.M. Lapchuk, E.N. Shumskaya, V.S. Varichenko, HELL&FD Lab., Belarussian State University, 220080 Minsk, Belarus
P-type (111) oriented 10 Ohm x cm silicon samples irradiated with 5.68 GeV Xe ions at doses within a range of 5×10^{11} to 5×10^{13} cm⁻² have been investigated with ESR technique. An intensive anisotropic line with g-value and width ranging from 2.4 to 10 and from 2800 to 3600 G respectively has been detected. Hysteresis loops of the spectra are observed when scanning the magnetic field up and down. The loss of magnetisation occurred during the spectra recording. The observed peculiarities are discussed in frame of a model based on spin-spin interactions emerging in silicon areas disordered by swift heavy ions.
- J-VII/P15** DWELL-TIME DEPENDENCE OF THE DEFECT ACCUMULATION IN FOCUSED ION BEAM SYNTHESIS OF CoSi₂, L. Bischoff, S. Hausmann, M. Voelskow and J. Teichert, Research Center Rossendorf Inc., P.O.Box 510119, 01314 Dresden, Germany
Cobalt disilicide microstructures were formed by 35 keV and 70 keV Co focused ion beam implantation into Si at substrate temperatures of about 400°C and a subsequent two step annealing (600°C, 60 min and 1000°C, 30 min in N₂). It was found that the CoSi₂ layer quality strongly depends on the pixel dwell time. Only for dwell-times of a few μ s continuous CoSi₂ layers could be obtained. To understand this effect scanning electron microscopy and Rutherford backscattering/channeling investigations combined with a special preparation technique for structures which are smaller than the analysing beam were carried out. The irradiation damage was measured as a function of dwell-time (1 - 250 μ s) and target temperature (370 - 430°C). The results showed that the accumulated irradiation damage increases with the dwell-time. The Si top layer was amorphized for longer dwell-times although the substrate temperature was always above the critical temperature for amorphization of about 270°C [1]. The results suggest that, due the high current density of the focused ion beam (1 - 10 A/cm²), the damage creation rate is higher than the rate of dynamic annealing.
[1] F.F. Morehead and B.L. Crowder, Rad. Eff. 6(1970)27.
- J-VII/P16** COMPARATIVE STUDY OF ION IMPLANTATION CAUSED DAMAGE DEPTH PROFILES IN POLYCRYSTALLINE AND SINGLE CRYSTALLINE SILICON STUDIED BY SPECTROSCOPIC ELLIPSOMETRY AND RUTHERFORD BACKSCATTERING SPECTROMETRY, P. Petrik, O. Polgar, T. Lohner, M. Fried, N.Q. Khanh, J. Gyulai, Research Institute for Technical Physics and Materials Science, P.O.B. 49, 1525 Budapest, Hungary; W. Lehnert, C. Schneider, H. Ryssele* Fraunhofer-Institut für Integrierte Schaltungen, Schottkystrasse 10, 91058 Erlangen, Germany; *Lehrstuhl für Elektronische Bauelemente, Friedrich-Alexander Universität Erlangen-Nürnberg, Cauerstrasse 6, 91058 Erlangen, Germany
Damage created by ion implantation of Ar⁺ ions into polycrystalline (p-Si) and single-crystalline silicon (c-Si) was characterized using Spectroscopic Ellipsometry (SE), Rutherford Backscattering Spectrometry (RBS), and Transmission Electron Microscopy (TEM). To create buried disorder, Ar⁺ ions with an energy of 100 keV were implanted into the samples. Ion doses were varied from 5.10^{13} to $6.75.10^{14}$. The parameters of the implantation were kept identical for both p-Si and c-Si. Damage depth profiles have been investigated using SE, RBS, and TEM, in case of c-Si, and SE and TEM in case of p-Si. The results prove the applicability of spectroscopic ellipsometry for characterizing ion implantation caused damage even in polycrystalline silicon, where the RBS method cannot be applied. The RBS and TEM results basically supported the optical model of SE.
- J-VII/P17** INVESTIGATION OF IONIC IMPLANTATION EFFECTS IN KTiOPO₄ (KTP) WAVEGUIDES BY REFLECTION SECOND HARMONIC GENERATION TECHNIQUE, P. Bindner, A. Boudrioua and J.C. Loulergue, MOPS-CLOES, Université de Metz et Supélec, Metz, France; P. Moretti, LPCML, URA CNRS 442, Université Claude Bernard-Lyon I, France; F. Laurell, Department of Physics, Royal Institute of Technology, Stockholm, Sweden
KTP is one of the most promising material to realize compact blue laser sources by second harmonic generation. Two main processes have been used in KTP crystals to elaborate optical planar waveguides: ionic exchange and ionic implantation. However, the nonlinearity of the guiding structure strongly depends on the fabrication process.
In this work we applied the reflection second harmonic generation technique to investigate light ions (H⁺ and He⁺) implantation effects in z-cut KTP crystals. In this configuration nonlinear properties of the guiding region are compared to those of the substrate.
No particular degradation of the non-linearity was observed in the He⁺ implanted KTP waveguides. Concerning the H⁺ implanted KTP crystal, a SH enhancement was detected around 100 μ m beneath the surface. This could be due to a possible modification of the crystal structure induced by the presence of the implanted protons in this area.
Beyond these results, these measurements point out the optical barrier position and its width in the crystal.
- J-VII/P18** INFLUENCE OF Ar⁺ IONS SPUTTERING ON THE CHEMICAL COMPOSITION OF SOME XEROGELS BASED ON VANADIUM OXIDES, V. Bondarenka, H. Tvardauskas, S. Grebinskij, Z. Martunas, S. Mickevicius, Semiconductor Physics Institute, A.Gostauto 11, 2600 Vilnius, Lithuania
The influence of Ar⁺ ions bombardment on the chemical composition of the vanadium xerogels (H₂V_{12-x}Mo_xO_{31+y}.nH₂O, H₂V₁₁TiO_{30.3}.nH₂O, H₂V_{12-x}Cr_xO_{31+y}.nH₂O, MV₁₂Mo_xO_{31+y}.nH₂O where M = Mg, Ca, Sr, Ba and M₂V₁₀Mo₂O_{31+y}.nH₂O where M = Li, Na, K) was investigated by means of X-ray photoelectron spectroscopy.
It has been found that before xerogels bombardment by Ar⁺ ions (E=3 keV, J=10 μ A/cm²) vanadium in all compounds is in V⁵⁺ and V⁴⁺ states. Other elements of the xerogels are in the highest valence states. After ionic bombardment the lower valency states of V, Mo, Cr the concentration of which increases with an increase of sputtering time were observed. Oxygen amounts decrease in all investigated compounds after bombardment. The conclusions about metal - oxygen binding energies in various xerogels and differences in their electrical conductivity were made.
- J-VII/P19** INVESTIGATION OF THE GETTERING OF IRON AND OXYGEN AT CAVITIES FORMED BY HELIUM ION IMPLANTATION IN CZ AND FZ SILICON, J.R. Kaschny, Instituto de Fisica, and P.F.P. Fichtner, Departamento de Metalurgia - UFRGS, 91501-970 Porto Alegre, Brasil; R.A. Yankov, W. Fukarek, A. Mücklich and W. Skorupa, Forschungszentrum Rossendorf, 01314 Dresden, Germany; A.B. Danilin, Centre for Analyses of Substances, 1 Electrodnaya Str., 111542 Moscow, Russia
Cavities formed in Si by He ion implantation and annealing are known to be strong traps for impurities and metal contaminants. The aim of this work is to study the binding of Fe to such cavities in CZ and FZ Si. The accumulation of Fe in the He-implanted layers was detected by SIMS. The cavities were characterized by XTEM, and their trapping efficiency was examined as a function of the annealing temperature, time and cooling rate. Direct comparison between the Fe depth profiles in CZ and FZ Si showed high gettering efficiency in both cases, and the profiles were correlated with the cavity distribution. Moreover, it was found that in CZ Si a significant amount of O was also trapped by the cavities. The O depth profiles exhibited two peaks located both sides of the buried cavity-containing layer, namely a small peak on the front (shallower) edge and a pronounced one at the back edge. The trapped O had no discernible influence on the gettering efficiency of Fe.

- J-VII/P20** IS THERE ANY IMPORTANT DEFECT LIFE AWAY FROM THE PEAK IN THE NUCLEAR ENERGY DEPOSITION PROFILE ?, R. Kögler, R.A. Yankov and W. Skorupa, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., POB 510119, 01314 Dresden, Germany

Although many problems around silicon as a key material of modern microelectronics are solved and many people believe to have a good understanding of this material, it has surprises in store yet. This concerns also problems of ion beam processing and related annealing. Recent experiments devoted to the investigation of gettering of unwanted metallic impurities at specific MeV implants showed that a Cu- or Fe- related decoration occurs not only, as is well-known, around the projected range of the implanted ions, R_p . Also there exist implantation and annealing conditions leading to maxima of decoration remote from the projected range. There can exist such sites at \sim half R_p or even deeper than R_p . These new and surprising results were mainly achieved via rapid thermal processing or conventional furnace annealing below 1000°C. Looking to the road-map of future silicon technology, maximum temperatures in the range of 800-900°C are allowed only. This points to the importance of these results. The origin of these defects is related to point defects and their clusters which get decorated by the fast diffusing metals. In this sense and apart from the problems related to technology, this defect decoration method provides a new and versatile tool to study the defect evolution concerned with ion beam processing and related annealing.

- J-VII/P21** HYDROGEN TRAPPING AT ION IMPLANTATION DEFECTS IN MgO, A. van Veen, H. Schut, A.V. Fedorov, IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands; E.A.C. Neeft, R.J.M. Konings, ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands, and B.J. Kooi, J.Th.M. de Hosson, Materials Science Centre, University Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Deuterium and hydrogen ions with energies varied from 15 keV to 30 keV have been implanted in virgin MgO (100) single crystals and in single crystals containing implantation generated noble gas (He, Ar) bubbles or Cu precipitates. Doses were varied from 10^{15} to 10^{16} cm $^{-2}$. The defects and the trapping of hydrogen at the defects were monitored by positron beam analysis. With this novel technique a depth distribution of defects can be determined for implantation depths from 0 to 2000 nm. Positrons have a high affinity to be trapped at sites with reduced atomic density like in vacancies and at precipitate-matrix interfaces. The character of the defects is related to deviations of the electron-momentum distribution observed as Doppler Broadening of the 511 keV annihilation gamma peak. It appeared that like in silicon hydrogen filled vacancies and vacancy clusters can be distinguished from the non-filled defects by the increase of annihilations with core electrons. This has been used to monitor arrival and dissociation of hydrogen release from a variety of trapping sites during hydrogen/deuterium implantation and subsequent annealing. Additional techniques used to provide information on the hydrogen and the defects were photon absorption, FTIR, high temperature hydrogen exposure, thermal gas desorption and HREM.

- J-VII/P22** CHARACTERIZATION AND SURFACE CRYSTALLIZATION OF AMORPHOUS $\text{Si}_{1-x}\text{Ge}_x$ INDUCED BY Ge ION IMPLANTATION INTO Si (100) SUBSTRATE, G. Peto, J. Kanski*, Z.F. Horvath, J. Gyulai, MTA Research Institute for Technical Physics and Materials Science, 1525 Budapest, P.O.Box 49, Hungary; *Physics Department of Chalmers Univ. of Technology, 41296 Göteborg, Sweden

$\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.5 - 5$ at%) was formed by Ge implantation with 80 keV energy into Si (100). The samples were characterized by angle resolved photoemission (ARUPS), LEED, and transmission electron microscopy (TEM). The valence band spectra from ion implanted amorphous Si-Ge deviated strongly from these data of a-Si and at $x = 5$ at% it was different from P implanted a-Si too. C or O concentration was under 1-2 at%. A transition (maybe amorphous-amorphous) was detectable on the surface at 400°C. An unreconstructed, crystallised surface was obtained by heating above 750°C. The outermost 20 nm layer was not epitaxial, the next 80 nm of the implanted layer showed defect free single crystal. These effects maybe explained by the properties of Ge implanted a-Si-Ge, which are markedly different from the normal a-Si. This surface regrowth strongly limits the possibility of defect free regrowth of ion implanted Si-Ge alloys. However, by a suitable removing of the nonepitaxial surface layer (e.g. by Ne ion bombardment) a good quality Si-Ge can be expected with Ge ion implantation into Si (100).

- J-VII/P23** A NOVEL $(\text{SiC})_{1-x}(\text{AlN})_x$ COMPOUND SYNTHESIZED USING ION BEAMS, J. Pezoldt, Institut für Festkörperelektronik, TU Ilmenau, PF 100565, 98684 Ilmenau, Germany; R.A. Yankov, A. Mücklich, W. Fukarek, H. Reuther, W. Skorupa, Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf e.V., PF 510119, 01314 Dresden, Germany

Wide-band-gap semiconductors based on the (SiC)-(III-N) material system are promising materials for advanced electronic, optoelectronic and sensor application. Of these compounds, the $(\text{SiC})_{1-x}(\text{AlN})_x$ system has been most extensively studied due to the full miscibility of SiC and AlN at temperatures above 1700°C, their good lattice and thermal matches, and the possibility of modifying the band gap of the resulting structure over a wide range of 2.2 eV (3C-SiC) to 6.2 eV (2H-AlN). To date, $(\text{AlN})_{1-x}(\text{SiC})_x$ solid solutions have been fabricated chiefly by either hot pressing or various deposition techniques. However, the crystal structure of the compounds so formed is constrained by thermodynamic equilibrium limitations. For example, at temperatures in excess of 1700°C the respective solid solution for $x=0.2$ will have the wurtzite structure (2H) and at lower temperatures the sphalerite (3C) form will be the favoured structure.

In this study we present results on the formation of a novel $(\text{AlN})_{1-x}(\text{SiC})_x$ compound ($x=0.2$) at lower temperatures within the miscibility gap of the AlN/SiC phase diagram by hot, high-dose high co-implantation of N^+ and Al^+ ions into 6H-SiC substrates. The compound layers have been studied by RBS/C, AES, PIRR and XTEM and the temperature dependence of their fabrication has been examined. An optimum temperature window has been established within which the structure of the synthesized material retains good crystallinity during implantation.

- J-VII/P24** MODIFICATION OF FREE CARRIERS CONCENTRATION IN ION- IMPLANTED SEMICONDUCTORS AS REVEALED BY INFRARED REFLECTIVITY, P. Lévêque and A. Declémy, Laboratoire de Métallurgie Physique, UMR 6630 CNRS, Université de Poitiers, BP 179, 86960 Futuroscope Cedex, France

Ion implantation is a widely used technique for the fabrication of shallow junctions in semiconductors. Nevertheless, the knowledge of ion-implantation damage in semiconductors has to be refined in order to control precisely this doping technique.

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ samples were implanted with low energy Al (320 keV) ions. Infrared reflectivity in the [2-20] μm range, combined with an original multilayer model provides interesting results on electrically active defects, like depth profile and free carriers concentration as a function of the implantation dose. High (He (0.8; 2 MeV)) and very high (Kr (750 MeV)) energy ion implantations have also been performed on II-VI $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ to validate the model used to fit experimental spectra. Other systems like SiC or III-V InSb implanted in various conditions have also been studied.

All these experiments show that infrared spectroscopy, which is a contactless and non destructive technique, can be used as a process control technique. When it is associated with a soft technique like diffuse X-ray-scattering, which is sensitive to the atoms displaced from their ideal lattice sites, it could also be a powerful tool to understand interactions between structural and electrically active defects created by ion implantation in semiconductors.

- J-VII/P25** NANOHARDNESS AND STRUCTURE OF NITROGEN IMPLANTED Si_xAl_y COATINGS POST-IMPLANTED WITH OXYGEN, M. Jacobs, F. Bodart, D. Schryvers*, A. Poulet**, LARN, FUNDP, 22 Rue Muzet, 5000 Namur, Belgium; *EMAT, University of Antwerp, RUCA, 171 Groenenborgerlaan, 2020 Antwerpen, Belgium; ** FPMS, 56 Rue de l'Épargne, 7000 Mons, Belgium
 "Sialons" have several interesting mechanical, thermal and chemical properties to make them candidates for high temperature applications. Solid solutions in the Si-Al-O-N system were synthesised using nitrogen and oxygen implantation into $\text{Si}_{30}\text{Al}_{70}$, $\text{Si}_{45}\text{Al}_{55}$ and $\text{Si}_{60}\text{Al}_{40}$ thin films deposited by DC magnetron sputtering on glassy carbon substrates: Nitrogen has been implanted firstly at 50 and then at 20 keV, oxygen were post implanted at 50 keV. The different implantation doses ranged from 1 to 10^{17} ions/cm². High depth resolution profiles and were obtained using RBS and resonant nuclear reaction, the chemical bonds were investigated using LEEIXS and these results are correlated to the film structure measured by cross section TEM. The TEM micrographs show a columnar structure perpendicular to the substrate surface in unimplanted coatings. Nevertheless when nitrogen is implanted grain formation is observed and after oxygen post-implantation gas bubbles appear at the film depth where the maximum oxygen concentration is observed. The correlation of these results with the RBS and LEEIXS measurements indicates that nitrogen should be enclosed in these bubbles. Nanohardness and Young's modulus were also measured. The highest values are observed in samples post-implanted with 10^{17} O/cm² where nanohardness increases from 3 to 10 GPa and Young's modulus from 70 to 100 GPa.
- J-VII/P26** ION BEAM MIXING OF METALS WITH SILICA, G. Rizza, J.C. Pivin, C.S.N.S.M., Bâtiment 108, 91405 Orsay Campus, France
 The ion beam mixing of thin metal layers (Ag, Au, Cu, Pd, Pt, W) embedded in a SiO_2 matrix was studied by means of RBS, XRD diffraction and TEM experiments. Irradiations were performed with increasing doses of Au ions, in the range of 10^{14} to 10^{16} /cm², at an energy of 4.5 MeV. The kinetics was studied as a function of the temperature, film thickness and depth. The first result of irradiation is to transform, at temperatures $\geq 273\text{K}$, the continuous metallic layer into a string of nanometer-sized metal inclusions. Different diffusion mechanisms are observed according to the temperature range: the variance of the mixed profile varies either as the square of the ion fluence or linearly with the fluence. The transition temperature depends on the metal. Saturation in the diffusion process is found when a critical amount of metal has dissolved. Alloying of metals has a catalytic effect on the diffusivity of one of them (for instance Ag in the case $\text{SiO}_2/\text{Ag-Au/SiO}_2$).
- J-VII/P27** As - Al RECOIL IMPLANTATION THROUGH Si_3N_4 BARRIER LAYER, P. Godignon, E. Morvan, J. Montserrat, X. Jordà, D. Flores, J. Rebollo, Centro Nacional de Microelectronica (CNM-CSIC), Campus UAB, 08193 Bellaterra, Spain
 Aluminum implantation is not always allowed in production set-up and can lead to technical problems and equipment degradation. Recoil implantation could be an alternative, and can be used to obtain double diffusion using n-type dopant as the incoming ion. As a result, a thin N^+ and deep P layers can be obtained to form bipolar or 4-layers devices. Another problem can result from the large Al exodiffusion coefficient and its high affinity with oxygen. Experiments of recoil implantation with As as implanted ion through an aluminium layer and a barrier layer (SiO_2 or Si_3N_4) have been performed. The thickness of the Al and the dielectric layers define the dose of Al and As which enter into the silicon. These thicknesses are optimized with Monte-Carlo simulations. SIMS and SRP measurements allow to study the implantation and annealing process. The comparison with other impurities makes As attractive due to its high atomic mass which results in a higher Al implanted dose. Results also showed that Si_3N_4 is the best choice as barrier layer since it limits the oxygen parasitic recoil implantation and it drastically reduces the exodiffusion of Al. A thin Si_3N_4 layer have been shown to prevent from the very high Al concentration at the silicon surface typical of recoil implantation, allowing a better Al activation and diffusion. It was also observed that for high As concentrations at the surface (thin Si_3N_4), active As dose increases with annealing time probably due to cluster dissolution.
- J-VII/P28** POLYMODALITY OF SIZE DISTRIBUTION FUNCTION OF Si NANOCLUSTERS IN SiO_2 , I.V. Blonskij, B.I. Lev, Institut of Physics, Ukrainian Academy of Sciences, pr. Nauki 46, 252028 Kiev, Ukraine
 The model, explaining experimentally observed polymodality of size distribution $F(R)$ function of Si nanoclusters in SiO_2 , is developed [1,2]. In the given model the manifestation of several maximums in the size distribution function is connected with nanocluster interaction in the size space, that is actual for supersaturated solutions. This interaction is being conducted by changing of local supersaturation field. In this case the coalescence process has the influence of "liquid phase". Physically it means that precipitated initially formed clusters in the case of high supersaturation effectively act upon the sizes of the newly formed ones. In the context of the model developed, based on the "liquid description" of nanocluster forming and time evolution, the cause of polymodality FCR), the deviation of the dependence $R(t)$ from the predicted $R=f(t^{1/3})$ and also some another kinetic characteristics are explained. The model developed combined with quantum- sized effect is also used to explain the discrete structure of Si in SiO_2 photoluminescence bands.
 Literature.
 1. T. Ngo, R. Williams. Appl. Phys. Lett., 1995, v. 66, N.15, p.1906.
 2. T. Komoda, J. Kelly, A. Nejim et al. Nuclear Instr. and Methods in Phys. Res., B96 (1995), p. 387.
- J-VII/P29** AFM AND STM INVESTIGATION OF CARBON NANOTUBES PRODUCED BY HIGH ENERGY ION IRRADIATION OF GRAPHITE, L.P. Biro*, G.I. Mark & J. Gyulai, Research Institute for Technical Physics & Materials Science, 1525 Budapest, POB. 49, Hungary; K. Havancsak, Eotvos University, 1088, Muzeum Krt. 6-8, Hungary; S. Lipp**, Ch. Lehrer, L. Frey & H. Ryssel, FhG-Institut für Integrierte Schaltungen IIS-B, 91058 Erlangen, Schottkystr. 10, Germany; *FUNDP, 5000 Namur, Rue de la Bruxelles 61, Belgium; **FEI-Europe GmbH, Bretonischer Ring 16, 85630 Grasbrunn, Germany
 Due to their remarkable properties, growing interest is focused onto the carbon nanotubes (CNT) since their discovery in 1991. Most of the CNT are produced by one of the three methods: electric arc, laser ablation, or catalytic decomposition of a gaseous hydrocarbon. We evidenced CNTs on graphite irradiated with low dose (10^{-12} cm⁻²), swift ($E > 100$ MeV), heavy (Ne, Kr, Xe) ions. It was found that the surface density of CNTs increases with the ion mass. In some cases CNTs were found which showed a regular vibration pattern when scanned with the AFM. In the case of Xe ions it was frequently found that the CNTs emerge from large area surface craters which are attributed to surface sputtering by dense nuclear cascades produced by higher order knocked on target atoms. We used a Focused Ion Beam (FIB) apparatus to cut CNTs and surface folds on graphite to be able to make a clear difference between these two types of structures.
- J-VII/P30** FORMATION OF COMPLEX Al-N-C LAYER IN ALUMINIUM BY SUCCESSIVE CARBON AND NITROGEN IMPLANTATION, V.V. Uglov, N.N. Cherenda, V.V. Khodasevich, Belarussian State University, pr. F. Scoriny 4, 220080 Minsk, Belarus; V.A. Sokol, I.I. Abramov, A.L. Danilyuk, Belarussian State University of Informatics and Radioelectronics, P.Browka 6, 220027 Minsk, Belarus; A. Wenzel, J.Gerlach, B. Rauschenbach, University of Augsburg, Institute of Physic, Memminger Str. 6, 86135 Augsburg, Germany
 The aim of this work was the investigation of composition and phase changes in aluminium after successive carbon and nitrogen implantation. The energy of ions was 40 keV, implantation doses varied in a range of $(3.3-6.5) \cdot 10^{17}$ ions/cm². The employed investigation techniques were TEM, RBS, AES (depth profiling and analysis of differential spectra). The existence of two main layers in aluminium was determined after successive implantation. First layer (thickness ~ 100 nm) was Al-N-C layer. The average C/N ratio was equal to 0.5 in it in case of maximum implantation doses. Only h.c.p. AlN structure was detected by TEM in this layer. The comparison of electrons energy in carbon KLL AES transition (270.0 ± 0.5 eV) in the layer with that in aluminium carbide (272.0 ± 0.5 eV) allowed to suppose C-N or C-C bond formation. Second layer (thickness ~ 75 nm) is Al_3C_3 layer formed in the depth of the sample by migrated carbon atoms. Maximum concentration of carbon in this layer was equal to 60 at. % for all doses of successive nitrogen implantation.

- J-VII/P31** ION-BEAM MODIFICATION OF a-SiO₂ and Ni/SiO₂-BILAYERS, M. Schwickert, W. Bolse, M. Gustafsson*, J. Keinonen*, K.P. Lieb, Universität Göttingen, II. Physikalisches Institut und Sonderforschungsbereich 345, Bunsenstrasse 7-9, 37073 Göttingen, Germany; *University of Helsinki, Accelerator Laboratory, P.O. Box 43, 00014 Helsinki, Finland

Modifications of thermally grown a-SiO₂ films and Ni/SiO₂ bilayers after irradiations with 350 keV Xe ions and subsequent thermal annealings in vacuum at 298-1173 K have been investigated. The analyses were performed by Rutherford backscattering spectroscopy (RBS) and surface profilometry. The homogeneity of the Ni films was controlled by optical and scanning electron microscopy. We here report on the ion-induced surface roughening and sputtering, the athermal ion-beam mixing at the Ni/SiO₂ interface and the swelling of the films. A low mixing rate in agreement with the ballistic model was found [1]. Very little Xe precipitation, which would indicate the presence of end-of-range spikes [2], was observed to occur at the interface. The rate of Xe loss during annealing was found to strongly depend on the implanted fluence.

[1] P. Sigmund, A. Gras-Marti, Nucl. Instr. and Meth., 182/183 (1981), 25.

[2] W. Bolse, T. Weber, Nucl. Instr. and Meth., B85 (1994), 188

- J-VII/P32** Ge ION IMPLANTATION FOR THE FORMATION OF Si/Ge_xSi_{1-x}, HETEROJUNCTION BIPOLAR TRANSISTORS, S. Lombardo, V. Privitera, and S.U. Campisano, CNR-IMETEM, stradale Primosole 50, 95121 Catania, Italy; A. Pinto and P. Ward, SGS-THOMSON, Catania, Italy

To fabricate fast Si/Ge_xSi_{1-x} heterojunction bipolar transistors (HBT), an interesting approach may be a technique based on high dose Ge ion implantation in Si followed by solid phase epitaxy, since ion implantation allows high wafer throughput and a perfectly planar process. For this purpose, we have investigated the structural quality of epitaxial Ge_xSi_{1-x} layers on (100) Si formed by high dose Ge implantation followed by rapid thermal annealing at 1000°C. It is shown that excellent quality can be achieved in terms of crystalline structure and contamination levels. Under the best Ge implantation conditions, we have fabricated Si/ Ge_xSi_{1-x} heterojunction n-p-n HBTs with two architectures, i.e., either with a self-aligned structure with polysilicon emitter and base contacts or a simpler structure with only the polysilicon emitter contact. Also the doping of the structures was performed by ion implantation and diffusion, by using As and BF₃ for emitter and base doping, respectively. It is shown that electrical performances are improved compared to reference Si transistors as a result of an effective band-gap engineering of the transistor base obtained by the Ge implant.

Wednesday June 17, 1998
 Mercredi 17 juin 1998

Afternoon
 Après-midi

SESSION VIII - Poster Session II
 17:00-18:30

- J-VIII/P1** COMPARATIVE STUDY OF ION IMPLANTATION CAUSED ANOMALOUS SURFACE DAMAGE IN SILICON STUDIED BY SPECTROSCOPIC ELLIPSOMETRY AND RUTHERFORD BACKSCATTERING SPECTROMETRY, T. Lohner, M. Fried, Q. Khanh, Research Institute for Technical Physics and Materials Science, 1525 Budapest, P.O.B. 49, Hungary; H. Wormeester, Faculty of Applied Physics, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands, M.A. El-Sherbiny, Faculty of Science, Al-Azhar University, Cairo, Egypt
 Damage created by ion implantation of 200 keV N⁺, 400 keV Ne⁺, 800 keV Ar⁺ and 900 keV Kr⁺ ions into single-crystalline silicon was characterized using Spectroscopic Ellipsometry (SE), Rutherford Backscattering Spectrometry (RBS) combined with channeling. Results both methods unambiguously show the presence of a heavily damaged thin layer at the surface which is not predicted by TRIM. The amorphization rate at the surface was found proportional to nuclear stopping power. It is demonstrated that SE cross-checked with RBS could be used for quantitative and accurate evaluation of the thickness of the damaged surface layer. The formation of this thin amorphous layer could be attributed to the redistribution of Si interstitials produced by the implantation process from the buried damaged region towards the surface and to a subsequent segregation process [1].
 [1] W. Fukarek, W. Moller, N. Hatzopoulos, DG Armour, and JA. van den Berg, Nuclear Instruments and Methods in Physics Research B 127/128 (1997) 879.
- J-VIII/P2** ION ASSISTED METALLISATION OF OXIDES BY IONIZED CLUSTER BEAMS, ELECTRICAL CONTACTS WITH HIGH ADHESION TO HTSC FILMS, A.S. Zolkin, Novosibirsk State University, 630090 Novosibirsk, Russia; A.V. Koshin and Yu. G. Shukhov, Institute of Laser Physics, 630090 Novosibirsk, Russia
 Thin metal films (10-500nm) with high density of covering, low-resistance contacts Ag/Y-Ba-Cu-O (10E-5 - 10E-8 Ohm cmE2) and high adhesion and stability to thermal shock (up to 20K) were fabricated by ICB. The vaporized material (Ag atoms and clusters up to 200 atom/cluster) from new metal vapour source [1] with vapour superheating (P=1000 Pa) is partially ionized by electrons (J(e)=100mA, E(e)=200 - 600eV) at the crucible exit where the vapour has its highest density and then ionized particles are accelerated in electric field (up to 10kV) and deposited (100 nm/min) on the substrate of HTSC/YBaCuO films, CdHgTe, ceramics, glass and metals. The plasma ion source (E/H, 1mA/cmE2, E(ion)=600-2000eV) was used for sputtering the degradation layer and for assistance during the deposition as the method for metallisation and preparing low-resistance contacts on the oxide of HTSC and devices of microelectronics.
 [1] Alexander S. Zolkin. J.Vac.Sci.Tecnol.A 15(3), May/Jun 1997, p. 1026.
- J-VIII/P3** RESIDUAL DEFECTS IN CZ-SILICON AFTER SELF-IMPLANTATION AND ANNEALING FROM 400°C TO 700°C, D.C. Schmidt*, B.G. Svensson**, J.F. Barbot*, C. Blanchard*, E. Ntsoenzok***, and S. Godey***, *Laboratoire de Métallurgie Physique, UMR 6630 CNRS, Faculté des Sciences, SP2M1, Bd3 Téléport 2, 86960 Futuroscope Cedex, France; **Department of Electronics, Royal Institute of Technology, Electrum 229, 16440 Kista-Stockholm, Sweden; ***CNRS-CERI, 3A rue de la Ferrollerie, 45071 Orléans Cedex, France
 Si(100) samples of n-type have been implanted with 5.6MeV ²⁸Si³⁺ at room temperature using a dose of 2x10¹⁸cm⁻². Thereafter the samples were annealed in nitrogen ambient for 30 minutes at temperatures from 400°C to 700°C using steps of 50°C. Deep level spectroscopy (DLTS) and capacitance voltage (C-V) measurements were used for sample analysis. Deep levels, not previously reported in the literature, are observed to arise, evolve, and to vanish again in the described temperature interval. Depth profiles of these levels show, that they are located beyond the projected range, as is characteristic for secondary implantation defects. The activation energies of these deep traps have been determined, and their possible identities are discussed, taking into account the existing literature concerning defects in this temperature range.
- J-VIII/P4** LOW FREQUENCY NOISE IN As IMPLANTED SILICIDES, M.M. Stojanovic, VINCA Institute of Nuclear Sciences, PO Box 522, 11001 Beograd, Yugoslavia
 Rapid development in microelectronics requires further upgrading of metal-semiconductor (M/S) contact structures, which should satisfy the strict criteria of dense packing, such as stability, reproducibility, susceptibility to other processing during device fabrication, etc. Silicides are widely investigated as promising reliable and reproducible contacts. The noise level measurements enable the control of the noise, which is important characteristic of metal-semiconductor (M/S) electrical contacts (especially 1/f noise). In our work we compare the RBS spectra and low frequency noise spectra of As⁺ implanted layers of TiN-Ti-Si structures, obtained in different conditions. Low frequency noise spectra are also obtained at different sample temperatures. Results of our measurements and analysis are of interest for solving the problems related to the application of ion implantation of As⁺ ions for the formation of silicides on p-Si, that are discussed by many authors in their investigations recently. It is known that the important characteristics of M/S electrical contact is their noise, specially that part of the noise (1/f noise) that depends on the surface effects (surface recombination fluctuations in carrier mobility, concentration of surface states, etc.).
- J-VIII/P5** MEASURING THE GENERATION LIFETIME PROFILE MODIFIED BY MeV H⁺ ION IMPLANTATION IN SILICON, N.Q. Khanh, Cs. Kovacsics*, T. Mohacsy, M. Adam, and J. Gyulai, KFKI Research Institute for Technical Physics and Materials Science, P.O.B. 49, 1525 Budapest, Hungary, *SEMILAB, Semiconductor Physics Laboratory RT, P.O.B. 18, 1327 Budapest, Hungary
 A silicon wedge mask with thickness varying from approximately 5µm to few hundred µm has been used for converting the changes in depth induced by 4 MeV H⁺ ion implantation in silicon (Rp~150 µm) to lateral scale on the surface. Thus, using the proper devices fabricated on bulk Si prior to ion implantation, depth profile of the generation lifetime of minority charge carrier and different traps can be measured by Zerbst method and Deep Level Transient Spectroscopy (DLTS), respectively. The distribution of lifetime follows well that of the implantation induced vacancy calculated by TRIM code in the applied dose range (from 1x10¹⁰ to 3x10¹¹ H⁺/cm²). Correlation between implantation dose and lifetime decrease, as well as increase of trap concentration are also discussed.

- J-VIII/P6** H⁺-IMPLANTATION EFFECTS ON THE ELECTRO-OPTIC COEFFICIENTS OF LiNbO₃ OPTICAL PLANAR WAVEGUIDE: DOSE INFLUENCE, A. Boudrioua, J.C. Loulergue, MOPS-CLOES, Université de Metz et Supélec, 57078 Metz, France; S. Ould. Salem, P. Moretti, LPCML, Université Claude Bernard Lyon I, 69622 Villeurbanne Cedex, France

The interest of waveguides into LiNbO₃ material reside, among others, in its electro-optic properties. However, the elaboration process effects on the waveguide electro-optic performances are not well overcome. Besides, the investigation of Ti diffused and He⁺ implanted LiNbO₃ waveguides showed a degradation of the electro-optic coefficients of about 70% and 30% respectively [1,2].

In this work, the electro-optic coefficients r_{13} and r_{33} of H⁺-implanted LiNbO₃ planar optical waveguides were measured using the guided modes angular shift when an electric field is applied to the sample. When using a gap between the deposited electrodes larger than the guiding layer thickness, the induced electric field into the guide can be considered as uniform, avoiding therefore fields overlap integral calculation. The investigation of the proton dose effect did not reveal any clear evolution of r_{13} and r_{33} values. Moreover, the obtained results are close to those reported in literature. This study shows that protons implantation in nonlinear materials is of great interest as their non-linear properties are preserved.

- J-VIII/P7** HIGH RESOLUTION EFTEM STUDY OF ION BEAM SYNTHESIS NICKEL SILICIDES, M.N. Yu, J.Y. Hsu, J.H. Liang, F.R. Chen, J.J. Kai, and L.C. Chen, Department of Engineering and System Science, National TsingHua University, Hsinchu, Taiwan 30043, R.O.C

The use of ion beam synthesis (IBS) in forming CoSi₂ films has been performed extensively in recent years. With a similar lattice parameter as that of CoSi₂, more recently, NiSi₂ has received increasing attention especially in micro-electronic devices applications. In the present study, NiSi₂ films were produced by implanting high-dose moderate-energy nickel ions into silicon wafers at elevated temperature and followed by annealing treatments. The implanted dose was 10^{17} ions/cm². The accelerated voltage was 40 kV and the charged states of the implanted nickel ions were 1⁺ (43%), 2⁺ (50%), and 3⁺ (7%). The silicon wafer was maintained at 200°C during implantation. After the implantation, the as-implanted specimens were annealed at 850°C from 30 seconds to 3 hours. Cross-sectional high resolution energy-filter transmission electron microscope (EFTEM) and nano-probe energy-dispersive spectrometer (EDS) were employed in the present study to analyze the evolution of NiSi₂ films. The results reveal that a four-layered structure with a depth of about 170 nm was formed in the as-implanted specimens. In the as-annealed specimens, octahedral (111)-faceted-island NiSi₂ precipitates, which possessing epitaxial (type A) relationship with the silicon substrate, were observed. In addition, the lateral dimension of NiSi₂ precipitates was increased with increasing annealing time. The cross-section areas of NiSi₂ precipitates were about 170x260 and 170x320 nm² for annealing time of 0.5 and 3.0 hours, respectively. A uniform distance of approximately 570 nm was found between NiSi₂ precipitates for annealing time of 0.5 hour. Notice that defected structures of silicon were existed between NiSi₂ precipitates. Several tiny NiSi₂ precipitates (~26x13 nm²) were embedded in the defected structures and located near the substrate surface. More detailed analyses are currently in progress and the results will be presented in the Conference.

- J-VIII/P8** BEHAVIOR OF IMPLANTED OXYGEN AND NITROGEN IN PULSE PHOTON ANNEALED SILICON, A.I. Belogorokhov, State Institute for Rare Metals, 5 B.Tolmachevsky per., 109017 Moscow; V.T. Bublik, K.D. Scherbachev, Y.N. Parkhomenko, Moscow Steel and Alloys Institute, 4 Leninsky Prospekt, 117936 Moscow; V.V. Makarov, A.B. Danilin, Centre for Analysis of Substances, 1/4 Sretensky Blvd., 103045 Moscow, Russia

The effect of mutual redistribution of implanted oxygen and nitrogen atoms at an early stage of high-temperature annealing is well-known. This effect allows buried silicon oxynitride layers to be obtained at relatively low total implantation doses. However, the nature of this mutual redistribution has not yet been clarified. To study this phenomenon, we have performed implantation of oxygen and nitrogen ions at substoichiometric doses, different energies and in different sequences. After implantation the samples were pulse photon annealed at 1200°C with 2-sec intervals. The samples were studied using FTIR, XRD and SIMS. We found that pulse photon annealing causes only slight mutual redistribution of the impurity, and a large number of thermally stable defect-impurity complexes, as well as phaseless chemical compounds form. Thus, it has been shown that phase formation due to mutual impurity redistribution depends strongly on sample heating and cooling during annealing.

The authors would like to acknowledge financial support from the Russian Fund for Basic Research, Grant # 95-03-08220.

- J-VIII/P9** EXTENDED DEFECTS IN Si WAFERS IMPLANTED BY IONS OF RARE-EARTH ELEMENTS, VI. Vdovin, Institute for Chemical Problems of Microelectronics, B. Tolmachevskii per. 5, Moscow 109017, Russia; T.G. Yugova, Institute of Rare Metals, B. Tolmachevskii per. 5, Moscow 109017, Russia; N.A. Sobolev, Ioffe Physico-technical Institute, Polytechnicheskaya 26, St.Petersburg 194021, Russia

A study of structural defect patterns in Cz-Si wafers implanted with ion-earth elements (Er, Ho, Dy) and annealed at high temperature (1000-1200°C) for 1/4-3h in a chlorine-containing ambience has been carried out. Ion implantation was performed at 1.0-1.8 MeV energy and 1×10^{13} cm⁻² dose. Structural defects were studied by chemical etching/Nomarski microscopy and transmission electron microscopy. Three types of defects, namely, Frank loops, perfect prismatic dislocation loops and pure edge dislocations were found to exist in the wafers. We studied the size and density of defects as well as defect distribution throughout the implanted region as functions of the implantation and annealing conditions. Evolution of the defect structure during the annealing was studied. We found that small Frank loops are generated at the initial stages. Some fraction of them gradually transforms into perfect dislocation loops. The interaction between large perfect loops crossing each other leads to the formation of pure edge dislocation segments. Long annealing of about 1h and more results in the formation of the well developed network of pure edge dislocations with density about 10^7 cm⁻².

- J-VIII/P10** MONTE CARLO SIMULATIONS OF Si PRECIPITATION IN Si-IMPLANTED SILICON DIOXIDE, A.F. Leier, L.N. Safronov, G.A. Kachurin, Inst. Semiconductor Physics, Novosibirsk 90, Russia

The opportunity for engineering Si light sources using quantum-size precipitates has attracted considerable attention. Si ion implantation into SiO₂ with subsequent annealing is believed to be the most promising way to form the light emitting Si nanoprecipitates. Although visible photoluminescence (PL) from Si-rich dioxide is reported by many authors the mechanism of the PL center formation is not well understood. It is established now that PL appears in as-implanted dioxide layers after implantation of several at.% of excess Si and changes its intensity and peak positions after anneals too weak for the diffusion-limited grain growth. The model is proposed explaining the changes in PL as multi-step segregation of the excess Si from SiO₂, including direct Si-Si bonding (blue PL), formation of Si percolation chains (PL in a wide spectral range), emergence of non-phase Si precipitates (orange PL), transformation of the precipitates in the amorphous phase inclusions (no PL), and, finally, growth of Si nanocrystals (strong red PL). The proposed model has been verified by the Monte Carlo 2D simulations taking into account the Si dose dependent probability for the direct Si-Si bonding and the temperature dependent development of Si percolation chains and clusters. The latter was evaluated via diffusivity of Si in SiO₂, as well as the transformation of the non-phase fractal type Si inclusions to the phase ones. The ion dose and annealing temperature ranges of the simulated processes are found to be in a good agreement with that obtained in the real experiments.

- J-VIII/P11** THERMAL REDISTRIBUTION OF IMPLANTED Al IN Si: EVIDENCES FOR INTERACTIONS WITH EXTENDED DEFECTS, Ch. Ortiz*, J.J. Grob*, D. Mathiot*, A. Claverie and R. Jérision**, CEMES-CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex, France; *PHASE-CNRS, 23 rue du Loess, BP 20, 67037 Strasbourg Cedex 2, France; **LMP (Univ. Tours), 16 rue P. et M. Curie, BP 7155, 37071 Tours Cedex 2, France
In the last years aluminium doping has been considered as a possible dopant in Si for high power devices applications. In this contribution we report on the results of a systematic study of the diffusion of implanted Al (180 keV, $4.5 \times 10^{14} \text{ cm}^{-2}$) during high temperature anneals. Various anneals were performed in the [900-1100°C] temperature range, for times varying from 15 min up to several hours. The SIMS profiles reveal anomalous redistribution of the aluminium profiles. The bulk side of the profiles diffuses normally at a rate in agreement with the Al intrinsic diffusivity, but two peaks of apparently immobile atoms are formed near the surface. As frequently observed for the redistribution of implanted dopants, one peak is located near the position of the projected range of the as-implanted Al. More surprisingly a second peak develops closer to the surface. The total dose of Al atoms immobilised in the peaks seems to depend only on the anneal temperature, independently of the anneal duration.
Cross observations by TEM prove that there is no Al precipitation, and reveal the existence of two extended defect bands, the position of which is perfectly correlated with the Al peaks. This strongly suggests that these peaks are due to Al trapping on the extended defects. First simulations support also this assumption.
- J-VIII/P12** ELECTRON MICROSCOPY AND ELECTROPHYSICAL INVESTIGATIONS OF THERMOINDUCED PROCESSES IN $\text{Ag-Cu}_x\text{Ni}_{1-x-y}\text{Co}_y\text{Mn}_{2-y}\text{O}_4$ SYSTEM, I.V. Hadzaman, M.M. Kravtsiv, Non-Linear Sensors Laboratory, Drohobych State Pedagogical Institute, 24 Iv. Franko Str., 293720 Drohobych, Lviv Region, Ukraine, O.Y. Mrooz and O.I. Shpotyuk, Institute of Materials, 202 Stryjska Str., 290031 Lviv, Ukraine
The processes which take place at the formation of Ag electrical contact in NTC thermistors on the base of $\text{Cu}_x\text{Ni}_{1-x-y}\text{Co}_y\text{Mn}_{2-y}\text{O}_4$ system are investigated.
The features of interaction on the border $\text{Ag-Cu}_x\text{Ni}_{1-x-y}\text{Co}_y\text{Mn}_{2-y}\text{O}_4$ are studied by the methods of electron microscopy (Jamp-10S and Camebax devices). It is established that intergrain boundaries may be presented as the phases with variable compositions where the non-stoichiometry defects play the main role. The maximum concentration of these defects is reached at the annealing of Ag contacts at $820 \pm 20 \text{ K}$ temperature. The decomposition and recrystallization processes in the material at this temperature range lead to the appearing of considerable thermoinduced diffusion of Ag from grain boundaries into the ceramic matrix. Reversible nature of this effect and correlation with electrical properties are established.
- J-VIII/P13** LIGHT PARTICLE IRRADIATION EFFECTS IN Si NANOCRYSTALS, G.A. Kachurin, S.G. Yanovskaya, K.S. Zhuravlev, A.K. Gutakovskiy, Institute of Semiconductor Physics, 630090 Novosibirsk, Russia, M.O. Ruault, CSNSM, 91405 Orsay Campus, France
Shrinking semiconductor device dimensions and the quantum-size effects in Si nanostructures have triggered interest in the study of radiation effects in Si nanocrystals. It is well known that structural stability and the melting point of nanocrystals essentially differ from those of the bulk material, thus their radiation tolerance should be thoroughly examined. In our experiments Si nanocrystals formed by the implantation of $10^{16} \text{ to } 10^{17} \text{ cm}^{-2} \text{ Si}^+$ ions in SiO_2 layers and by the subsequent annealing at 1150°C for 30 min have been irradiated with the 30-100 keV He^+ ions and with 400 keV electrons in the TEM column. Room temperature photoluminescence in the visible range and in-situ TEM were carried out as a function of the irradiation dose and of the annealing temperature. Strong red emission, usually ascribed to the quantum-size Si nanocrystals, has been found to decrease and vanish after He^+ bombardment within the dose range of $10^{12} \text{ to } 3 \cdot 10^{13} \text{ cm}^{-2}$. The disappearance of the red band was accompanied with the increase in the short-wavelength emission. TEM has shown the disappearance of Si nanocrystals after He^+ irradiation and partially after irradiation with the fast electrons. In both cases the elastic energy deposited within the nanocrystals was much lower than the minimal level required for the amorphization of bulk silicon. Anneals up to 775°C were found to be unable to recrystallize the nanostructures. The reasons for the effects observed are discussed.
- J-VIII/P14** PECULIARITIES OF DEFECT GENERATION IN Si^+ -IMPLANTED GaAs (211) WAFERS, S.B. Evgeniev, A.A. Kalinin, M.G. Mil'vidskii, Institute for Chemical Problems of Microelectronics, B.Tolmachevskiy pr. 5, 109017 Moscow, Russia, V.T. Bublik, A.W. Nemirovskii, Moscow State Steel and Alloys Institute, Leningrad pr. 4, 117571 Moscow, Russia
Peculiarities of defect generation in GaAs (211) wafers after Si ions implantation with doses below than that for GaAs amorphization have been studied by X-ray diffraction, secondary ions mass-spectroscopy and transmission electron microscopy. The degree of lattice damage due to radiation defects was found to depend on wafer orientation so that it is more less in (211) wafers than in (100) ones. These defects are easily annealed during rapid photon annealing in (211) wafers. Along with these two effects we observed the more deep penetration of implanted ions in (211) wafers. Relaxation of implantation-related excess point defects does not accompany by dislocation formation in (211) wafers as it occurs in (100) wafers. The findings indicate that there is no difference between [110] and $[\bar{1}\bar{1}0]$ directions in point of defect formation and relaxation.
- J-VIII/P15** THE COMPARISON OF OPTICAL AND PHOTOLUMINESCENCE PROPERTIES OF SiO_2 LAYERS IMPLANTED WITH SILICON AND SILICON+PHOSPHORUS AT HIGH DOSES, D.I. Tetelbaum, O.N. Gorshkov, E.S. Demidov, S.A. Trushin, M.V. Stepikhova, Physico-Technical Research Institute of University of Nizhniy Novgorod, Gagarin prosp., 23/3, 603600 Nizhniy Novgorod, Russia
The SiO_2 :Si nanostructures system attracts great attention due to its promising for optoelectronics properties. Ion implantation is not only the suitable way for production but essentially unique method for doping of such a system. The SiO_2 :Si layers were formed by ion implantation of 150 keV Si^+ into SiO_2 films on Si, or into fused silica (doses $1 \cdot 10^{17}$ to $5 \cdot 10^{17} \text{ cm}^{-2}$). One part of the samples were implanted additionally with P^+ . The doses corresponded to several P atoms per Si inclusion. For the as implanted layers, optical bandgap is reduced, refractive indexes are higher than for initial SiO_2 , and additional ESR-centres are appear. The photoluminescence spectra depend of the exciting light wavelengths λ_{ex} , the peaks being locate at approximately 600 and 800 nm for $\lambda_{\text{ex}} = 351$ and 488 nm respectively. The additional phosphorus implantation intensifies the PL. It is suggested that the influence phosphorus is caused by the equilibrium filling of levels in conduction band of Si nanoinclusions (quantum dots).
- J-VIII/P16** ION IMPLANTATION OF Be AND Se INTO GaAs(100) AT GRAZING INCIDENCE, A.A. Dzhrakhalov and I.I. Khafizov, Institute of Electronics, 700143 Tashkent, Uzbekistan
The peculiarities of processes of the low-energy ion implantation of Be and Se into GaAs(100) at grazing incidence have been investigated by computer simulation in binary collision approximation using the code which is similar by its structure to the well-known MARLOWE program. The ion energies were 1,5 keV.
The implanted depth distributions of the Be, an acceptor in GaAs, and Se, a donor in GaAs, for a range of grazing angles of incidence (3-20 degrees) at different crystal orientation ($\langle 110 \rangle$, $\langle 100 \rangle$) have been calculated and compared.
It was shown that the profiles depend on the ion mass and energy, the crystal orientation and the angle of incidence. At sufficiently small grazing angles smaller than a critical angle, corresponding to the threshold of ion penetration the ion implantation processes do not take place due to impossibility of ion penetration through surface. Value of the critical angle decreases slightly with increasing initial energy and decreasing mass of incident ion. At grazing incidence the ions of primary beam penetrate in several nearest to surface atomic layers during the process of their movement in channels of low index directions along surface. Therefore in this case the main peak of the implanted depth distributions is considerably shallower than that for normal incidence. With increasing grazing angles the peak of profiles is slightly shifted in the field of deep layers. It was shown that the range for Se is shallower than that for Be and the half-width of profile for Se is narrow.

- J-VIII/P17** INFLUENCE OF ION BEAM CURRENT DENSITY ON PHASE FORMATION OF CoSi₂ BURIED LAYERS, Yu.N. Parkhomenko, K.D. Chitchevatchev, A.A. Galaev, A.B. Danilin, Moscow State Institute of Steel and Alloys, 4 Leninskii Pr., 117936 Moscow, Russia and A. Perez-Rodriguez, A. Romano-Rodriguez, A. Dieguez, J.R. Morante, Universitat de Barcelona, A.Diagonal 645-647, 08028 Barcelona, Spain

The influence of ion beam current density to phase formation of CoSi₂ buried conductive layers was studied by SIMS, XPS, XRD, HREM and AFM methods. The layers were directly synthesized by IBS method at 180keV, $2 \cdot 10^{17} \text{ cm}^{-2}$ dose and various ion beam current densities (5, 15 and $30 \mu\text{A} \cdot \text{cm}^{-2}$). Continuous heteroepitaxial CoSi₂ layer with thickness of 90 nm at the depth of 100 nm is formed just after implantation with beam current density of $15 \mu\text{A} \cdot \text{cm}^{-2}$. Interstitial-type defects that located just under CoSi₂ layer were revealed in all as implanted samples. After 1150°C 30min annealing the defects only remained in the sample corresponded to the highest density of ion beam current ($30 \mu\text{A} \cdot \text{cm}^{-2}$). The best electric parameters were achieved for the samples synthesized at ion beam current density of $15 \mu\text{A} \cdot \text{cm}^{-2}$.

- J-VIII/P18** LATTICE LOCATION AND ANNEALING BEHAVIOUR OF Pt AND W IMPLANTED SAPPHIRE. E. Alves, R.C. Silva, M.F. da Silva, J.C. Soares*, Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2685 Sacavém, Portugal; *CFNUL, Univ. Lisboa, Av. Prof. Gama Pinto 2, 1699 Lisboa, Portugal

Sapphire ($\alpha\text{-Al}_2\text{O}_3$) single crystals were implanted with different doses of Pt and W ions in the range of 10^{14} to 10^{17} at/cm^2 at room temperature. Detailed angular scans through the main axial directions show that up to doses of the order of 10^{15} at/cm^2 about 70% of the W and Pt ions were incorporated into substitutional or near substitutional lattice sites. The implantation damage show a double peak structure, being one peak at the surface and the other at the end of the implantation range. The overlap of these two damage peaks, which indicates the amorphization of the implanted region, starts for doses of the order of $1 \times 10^{16} \text{ at/cm}^2$. The surface damage anneals out at low temperature (800°C) while the deeper damage needs much higher temperatures. Even after annealing at 1400°C there is some damage remaining. The amorphous state regrows epitaxially during the annealings in vacuum at high temperatures, with a velocity of 3 Å/min at 1100°C. The regrowth stops when the amorphous/crystalline interface reaches the region of the maximum concentration of the implanted ions. When the annealing is done at ambient atmosphere the damage recovers completely at 1100°C even for doses of the order or $5 \times 10^{16} \text{ at/cm}^2$. In this case the formation of Pt precipitates is observed. The correlation of the structural changes produced by the implantation with the electrical properties of the crystals will be discussed.

- J-VIII/P19** MICROGETTERING OF PLATINUM IN PROTON IRRADIATED SILICON, D.C. Schmidt***, B.G. Svensson**, J.F. Barbot*, C. Blanchard*, E. Ntsoenzok***, S. Godey***, and N. Keskitalo**, *Laboratoire de Métallurgie Physique UMR 6630 CNRS, Faculté des Sciences, SP2MI, Bd3 Téléport 2, 86960 Futuroscope Cedex, France, **Department of Electronics, Royal Institute of Technology, Electrum 229, 16440 Kista-Stockholm, Sweden, ***CNRS-CERI, 3A, rue de la Férollerie, 45071 Orléans Cedex, France

Epitaxial silicon samples of n-type have been implanted with 850 keV protons at doses of $5.8 \times 10^{11} \text{ H}^+ \cdot \text{cm}^{-2}$ to $5 \times 10^{13} \text{ H}^+ \cdot \text{cm}^{-2}$. Subsequent in-diffusion of platinum at 700°C for 30 minutes resulted in the presence of a single deep level, which is attributed to the platinum acceptor level at 0.23eV below the conduction band edge. Depth profiling of this level has shown, that the substitutional platinum is following the vacancy profile in the peak region around the projected range for the protons. In addition, at more shallow depths a strong increase of the platinum concentration is also observed. Without ion-implantation, no deep levels are detected after in-diffusion at 700°C, while at 800°C, the Pt deep level concentration is inferior to the one reached after pre-implantation of hydrogen with a dose of at least $5 \times 10^{12} \text{ H}^+ \cdot \text{cm}^{-2}$. In-diffusion at 600°C into $5 \times 10^{13} \text{ H}^+ \cdot \text{cm}^{-2}$ implanted samples did not lead to an enhanced platinum accumulation. A tentative explanation of this 'microgettering' of Pt is proposed, which is for the first time observed after light-ion irradiation.

- J-VIII/P20** EPR STUDY OF α -Si STRUCTURAL RELAXATIONS, B. Pivac, B. Rakvin, Ruder Boskovic Institute, P.O.Box 1016, 10000 Zagreb, Croatia and R. Reitano, Instituto Nazionale di Fisica della Materia-Unitadi Catania, Corso Italia 57, 95129 Catania, Italy

Structural relaxation in disordered solids, and particularly for α -Si is of particular importance, since it has been shown that some physical properties like low-temperature diffusivity and solid solubility of several elements depend on the degree of relaxation of the amorphous material. In this paper it will be shown that EPR spectroscopy is an effective method for the study of relaxation and derelaxation process.

α -Si is prepared by Kr⁺ ion implantation in Si. Samples were subsequently relaxed by thermal treatment and derelaxed again by ion implantation. EPR analysis has shown that the concentration of dangling bonds is significantly reduced in relaxed state, indicating increased ordering. On the other hand during derelaxation, it proportionally increases along with disordering. In this way a macroscopical information on bulk disorder is obtained. Moreover, the analysis of the line profile variation, of D-centers, shows that relaxation widens EPR line, while subsequent derelaxation reduces it again. This finding is in accordance with cluster model¹ of α -Si prepared by ion implantation. Therefore, it is shown that EPR gives both macroscopical and microscopical information on disorder in material. Results are discussed in the light of current models for amorphisation process by ion implantation.

B.Rakvin, B.Pivac, and R.Reitano, J. Appl. Phys. **81**, 3453 (1997).

- J-VIII/P21** PD-DIFFUSION IN ZnTe AND CdTe, S. Hermann, H.-E. Mahnke, B. Spellmeyer, HMI Berlin GmbH, 14109 Berlin, M. Wienecke, B. Reinhold, HU Berlin, Institut für Physik, 10115 Berlin, Germany; R.A. Yankov, FZ Rossendorf, 01314 Dresden, Germany and H.-E. Gumlich, TU Berlin, Institut für Festkörperphysik, 10623 Berlin, Germany

The diffusion of ¹⁰⁰Pd was studied in metal- and tellurium-rich ZnTe and CdTe, resp., with radioactive tracer techniques. The radioactive ¹⁰⁰Pd atoms were produced at the Ionbeam-Laboratory ISL of the HMI by heavy-ion nuclear reactions and recoil-implanted into the samples up to a depth of 4µm. Some of the samples were predoped with group-V elements by implantation at the FZ Rossendorf up to the same depth. For tellurium-rich material, subsequent annealing for 20min at 900 K results in two fractions of Pd, with roughly equal amounts, one fraction of Pd pinned in the implantation region, and the second fraction distributed through the whole sample of 500µm thickness. This diffusion behaviour is unchanged by additionally implanted e.g. N. Metal-rich material shows a completely different diffusion behaviour of Pd: Pd becomes fully distributed over the whole samples when no additional group-V element is implanted; additional implantation of group-V element again leads to pinning in the case of ZnTe, but not in CdTe. An extracted diffusion constant for the unhindered Pd diffusion in ZnTe and CdTe is of similar size as known for fast interstitial diffusion of Pd in Si. With PAC techniques various Pd-defect-complexes have been identified for pinned Pd as well as in the case of CdTe for a Pd-N complex following the fast diffusion and quenching to room temperature.

- J-VIII/P22** ELECTRICAL AND OPTICAL PROPERTIES OF $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ ALLOYS AFTER Co⁺ ION IMPLANTATION, B. Sealy, R. Gwilliam, J. Shannon, C. Jeynes, Depart. of Elect. and Electrical Engineering, University of Surrey, Guilford, Surrey, UK; T. Tsvetkova, Inst. Solid State Phys., Bulg. Acad. Sci., N.Tzenov and D. Dimova-Malinovska CLSENEs, Bulg. Acad. Sci., 1784 Sofia, Bulgaria

Considerable drop of the resistivity of $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloy films was observed after high doses of Co⁺ implantation. Thus high values of the conductivity, increased by orders of magnitude, were obtained and even further improved by different annealing procedures. The influence of the carbon content in the Co⁺ implanted $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ films on the electrical modification effect was studied. The greatest conductivity changes were observed in the $\alpha\text{-Si:H}$ samples and still further decrease of the resistivity (up to 50%) was found upon subsequent annealing treatments. The accompanying modification effect on the optical and structural properties were studied by means of optical, IR and Raman spectroscopy. These effects could be related to the structural modification and possible emergence of new CoSi₂ phase as seen by IR and Raman spectroscopy results. Deposition technique and incorporated hydrogen effect on the sputtering rate of the implanted samples was registered.

- J-VIII/P23** **SYNTHESIS OF SINGLE-CRYSTALLINE AL LAYERS IN SAPPHIRE**, W. Schlosser, J.K.N. Lindner, M. Zeitler and B. Stritzker, Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany
The formation of buried aluminium layers in Al_2O_3 crystals by high-dose implantation of Al^+ ions is studied. For this purpose, 180 keV Al^+ ions were implanted at constant temperatures between 300 and 500°C into c-plane (0001) and r-plane (1102) sapphire crystals with doses of $1.5\text{--}12 \times 10^{17} \text{ Al/cm}^2$. The samples were characterized with x-ray diffraction (XRD), x-ray pole figure measurements, Rutherford Backscattering Spectroscopy (RBS), cross-section transmission electron microscopy (XTEM), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).
XRD and XTEM show the formation of a buried single-crystalline Al-layer in c-plane sapphire at sufficiently high doses directly after implantation. The layer exhibits an epitaxial relationship with the sapphire matrix as $\text{Al}(111) \parallel \text{Al}_2\text{O}_3(0001)$ and $\text{Al}[011] \parallel \text{Al}_2\text{O}_3[1100]$. The layers are approximately 100 nm thick and covered with 170 nm of damaged but crystalline Al_2O_3 . The layer thickness is observed to vary significantly, while the interfaces are surprisingly sharp. RBS investigations reveal that the retained amount of Al in these layers is considerably smaller than the implanted dose. SEM/EDX studies demonstrate the formation of spherical Al particles with diameters of up to 250 μm on the surface. From studies of the Al precipitate formation at lower doses, insight into the mechanisms leading to the formation of homogeneous buried c-Al layers is gained.
- J-VIII/P24** **MODIFICATION OF SOLIDS AND SELF-ORGANIZING PROCESSES INDUCED BY LOW-ENERGY ION IRRADIATION**, I.V. Tereshko, V.I. Khodyrev, A.A. Russian, J.V. Rimkevich, D.L. Vinogradov, Mechanical Engineering Institute, 212005 Mogilev, Belarus.
The subject of investigation were armco-iron, metal-ceramic hard alloys with the composition of 79% tungsten carbide (WC) and 15% of titanium carbide (TiC) and samples of graphite with copper and lead impurities. All samples were exposed to gas discharge plasma under the voltage of 0.8–2.5 kV, samples being irradiated by ions of residual gases of vacuum. The ion energy depended on the voltage in the plasmagenerator and did not exceed 0.8–2.5 keV.
We showed that the process of low-energy influence led to the increase in the dislocation density up to 10 mm in depth from the irradiated surface. This is actually a bulk modification. This result was described as a "long-range effect" (LRE). LRE is displayed mostly in unannealed samples with exceedingly high initial heterogeneous dislocation structure. The microhardness varies greatly with the time that elapsed after stopping the external influence and it is chaotically oscillating. The change in ion energy can lead to both strengthening and plasticity increase in samples. These modifications in materials could be understood within the conception of active self-organizing processes in crystal lattices. The authors suggest a hypothesis based on the idea of nonlinear oscillation excitation in the ion subsystem of crystals.
- J-VIII/P25** **ELECTROCATALYSIS OF OXYGEN REDUCTION ON ELECTROCERAMICS BY IMPLANTED TRANSITION METALS**, A.J. McEvoy, J. Van Herle, S. Widmer* and T. Tate**, Laboratory for Photonics and Interfaces, Department of Chemistry, Ecole Polytechnique Federale de Lausanne, 1015 Lausanne, Switzerland; *Forschungszentrum Jülich, Germany; **Imperial College, London, UK
The solid oxide fuel cell is under development for environment-friendly small scale combined heat and power (CHP) installations. On the cathode side of such a fuel cell, oxygen from the air is reduced to oxygen ions at the interface between two electroceramics, an electronically conducting perovskite electrode and a solid electrolyte, normally yttria-stabilised zirconia, in which electrical conductivity is due to mobile oxygen ions only. Polarisation of the electrode-electrolyte interface is a major loss mechanism, and considerable effort has gone into its nanostructuring and electrocatalysis. By ion implantation a known dose and concentration profile of electrocatalytically active elements, particularly Mn and Ce, can be inserted in the near-interface zone of the zirconia, permitting the determination of the mechanism of the accelerated charge transfer and indicating a strategy for the fabrication of more efficient fuel cells.
- J-VIII/P26** **STABILITY STUDIES OF Hg IMPLANTED YBCO THIN FILMS**, J.P. Araujo, V.S. Amaral, J.B. Sousa, Dep. Física, FCUP, Rua do Campo Alegre 687, 4150 Porto, Portugal; A.A. Lourenço, INESC, Rua Campo Alegre 687, 4150 Porto, and Dep. Física, FCUA, 3800 Aveiro, Portugal; E. Alves, J.G. Marques, J.C. Soares, CFNUL, Av. Prof. Gama Pinto 2, 1699 Lisboa Codex, Portugal; A. Vantomme, U. Wahl, University of Leuven, Instituut voor Kern- en Stralingsfysica, Celestijnenlaan 200 D, 3001 Leuven, Belgium; V. Galindo, T. Papen, J.P. Senateur, F. Weiss, UMR CNRS 5628, INPG-ENSPG, BP 46, 38402 St. Martin D'Hères Cedex, France; J.G. Correia and the ISOLDE Collaboration, CERN, 1211 Genève 23, Switzerland
High quality $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) superconducting thin films were implanted with the radioactive $^{197\text{m}}\text{Hg}$ ($T_{1/2}=24\text{h}$) isotope to low doses of 10^{13}at/cm^2 , and 60keV energy at ISOLDE/CERN. By using the perturbed angular correlation (PAC) and the emission channeling (EC) techniques the Hg stability and lattice sites were studied, respectively. We show that Hg can be introduced into the YBCO lattice by ion implantation, being able to find one unique regular site already in the as-implanted state. The preliminary analysis of the EC data shows that mercury sits on a highly symmetric site on the YBCO lattice. The PAC data strongly suggests that Hg occupies the Cu(1) site, in agreement with the fact that Hg has a big affinity to form linear-like coordinated bonds with oxygen. Annealing studies were performed under vacuum and O_2 atmosphere. It has been further shown that the implanted Hg stays into the YBCO lattice up to 500 °C. The influence on the YBCO transport properties of Hg, implantation defects, and annealing treatments was studied with the alternate susceptibility (χ_{ac}) technique. The possibility of using the PAC technique with the $^{197\text{m}}\text{Hg}$ isotope to probe the phase transition and defects is presented and discussed.
- J-VIII/P27** **MODIFICATION OF A POST-IMPLANTATION DEFECT ACTIVITY FOR PHOTOVOLTAIC CONVERSION**, Z.T. Kuznicki, CNRS, Laboratoire PHASE (UPR 292), BP 20, 67037 Strasbourg Cedex 2, France
The problem of an eventual usefulness of defects and traps in solar cells (and especially in implanted Si material) has been investigated since the 1980s. Usually in place of increase, the efficiency actually diminishes because of the increased non-radiative recombination on numerous defects. At the beginning of the 1990s a new approach can be observed, which distinguishes between the microelectronic and photovoltaic points of view on the possible usefulness of post-implantation defects. The fundamental difference concerns the thermodynamic aspects of the two types of devices: microelectronic and photovoltaic which differentiates a receiver and a generator from the electronic point of view. In the solar cell there is an additional dimension, i.e. optoelectronic properties where the electronic behavior (recombination) can be completed/modified by an optical activity (generation).
For example, damaged Si reduces the free carrier lifetime which has repercussions on the carrier density. But if the same damaged material can be placed in an electric field (drawing out the generated carriers) the corresponding lifetime and, as a consequence, the carrier density can increase considerably. We have analyzed theoretically and experimentally some possible modifications of the post-implantation defect activity on single-crystal Si in view of the very- and ultra-high PV conversion efficiency.

- J-VIII/P28** INVESTIGATIONS OF ION BEAM MIXING EFFECTS IN Ta THIN FILMS ON Si SUBSTRATES, N. Bibic, M. Milosavljevic, D. Peruvsko, VINCA Institute of Nuclear Sciences, 11001 Belgrade, P.O.Box 522, Yugoslavia; and C. Jeynes, Dept. of Electronic and Electrical Eng. University of Surrey, Guildford, Surrey GU2 5XH, UK
This paper presents a study of As^+ and Xe^+ ion irradiation influence on Ta thin films on silicon substrates. Thin Ta films were deposited on (100) Si to the thickness of 50, 70 and 110 nm, by d.c. ion sputtering. The Ta/Si structures were implanted at room temperature with 350 keV As^+ and 300 keV Xe^+ ions to the doses from 1×10^{15} to 2.5×10^{16} ions cm^{-2} . The different Ta layer thickness and the different implanted species gave a variety of the ion ranges with respect to the depth of the Ta/Si interface. Characterization of samples included Rutherford backscattering spectroscopy (RBS), X-ray diffraction spectrometry (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). We have studied the effects of the ion species, ranges and doses on the reactions in Ta/Si structures. The results have shown that intermixing of components at Ta/Si interface has occurred practically for all implanted doses. For higher ion doses and thinner Ta layers the formation of Ta-silicide phases is completed as in the case of thermal annealing. Although during thermal diffusion Ta-silicides are formed at high temperatures, above 900°C, their behaviour during ion beam mixing is similar as in the cases of low temperature forming metal-silicides.
- J-VIII/P29** FORMATION OF THIN SILICON NITRIDE LAYERS ON Si BY LOW ENERGY N_2^+ ION BOMBARDMENT, V.I. Bachurin, A.B. Churilov, E.V. Potapov, Y.K. Smirnov, Institute of Microelectronics of RAS, Krasnoborskaya str. 3, 150051, Yaroslavl, Russia; V.V. Makarov, A.B. Danilin, Center for Analysis of Substances, 1/4 Sretensky Blvd, 103045 Moscow, Russia
Silicon nitride dielectric layers have a number of attractive characteristics for microelectronics, but they have not yet found general use because of the insufficient quality of Si_3N_4 thin films obtained using the chemical vapor deposition (CVD) method. These films contain surplus silicon and impurities from reagents in CVD process. A promising alternative way is to produce Si_3N_4 thin films by nitrogen ion implantation into silicon. In this case it is possible to avoid the impurities and to control the composition, structure and thickness of the films by varying the experimental conditions.
We present results on the formation of silicon nitride on Si by N_2^+ ion bombardment. The implantation into (100) silicon wafer was carried out in a UHV chamber at 20-750 sondzeichen 176 f "Symbol".C using 3-9 keV N_2^+ ion beams with fluences ranging from 2 sondzeichen 180 f "Symbol" 1015 to 1 sondzeichen 180 f "Symbol" 1018 cm^{-2} at 0-70 sondzeichen 176 f "Symbol" incidence angles. The samples were examined using AES, SIMS and FTIR to explore the composition, structure and thickness of Si layers modified by ion implantation.
It was shown that the formation of amorphous stoichiometric Si_3N_4 near the surface depends on ion beam incidence angles and begins from fluences of 2 sondzeichen 180 f "Symbol" 1017 cm^{-2} . The influence of implantation conditions on silicon nitride parameters was studied and discussed.
This work was supported by RFBR (Grant No. 96-02-18541)
- J-VIII/P30** ANOMALOUS FIELD DEPENDENCE OF DEEP LEVEL EMISSION IN PROTON IRRADIATED SILICON, N. Keskitalo, A. Hallen, P. Pellegrino, and B. Svensson, Royal Institute of Technology, Dept. of Electronics, P.O. Box E229, 16440 Kista-Stockholm, Sweden
In this study n-type silicon with doping ranging from 10^{10} cm^{-3} up to 10^{16} cm^{-3} have been irradiated with protons of energies from 1.3 MeV to 9.5 MeV. The proton doses have been restricted to levels that results in point defect concentration below 10% of the doping at the investigated depths in the samples. This makes quantitative analyses with deep level transient spectroscopy possible and depth profiling of defect concentrations have been performed, both by single and double pulse techniques. The depth of interest are in the tail of the defect distribution close to the surface and far from the projected range of the protons. In this region an almost uniform defect concentration is expected. Only a slight increase should be measured when moving deeper into the sample. However, a dramatic drop in the defect concentration is measured when a high electric field is present, as was the case for the 10^{16} cm^{-3} samples (20 kV/cm). The anomalous field effect is especially prominent for the well known vacancy-oxygen center and the singly negative charge state of the divacancy, both acceptor levels that should not display a Poole-Frenkel effect.
- J-VIII/P31** GROWTH AND CHARACTERIZATION OF Ge NANOCRYSTALS, S. Guha, Naval Research Laboratory, Washington DC., USA, and L.L. Chase, Lawrence Livermore National Laboratory, Livermore CA, USA
Ge nanocrystals are grown by ion-implantation into SiO_2 films and subsequent annealing. Ge-ions at 190 keV to a dose of 1, 2, and 3×10^{17} cm^{-2} are implanted into a thermally oxidized Si films of thickness 500 nm. After annealing at 830 C in N_2 atmosphere for 30 min, three different average particle sizes are observed in these three films: 12 nm for 3×10^{17} , 8 nm for 2×10^{17} , and 4 nm for 1×10^{17} . Electron spin resonance measurements detect no paramagnetic centers in these annealed samples. Raman scattering experiment detects a phonon band at 298 cm^{-1} . For a certain excitation wavelength, the peak position of this phonon band is identical in all three films, inspite of their different particle sizes. However the width of the Raman band was found to vary in these three samples with the excitation wavelength. This observation leads us to believe that there is a distribution of particle size in these films, and the excitation wavelength resonantly excites a particle of certain size in these films. A model will be presented to estimate the particle size. The origin of a blue (420 nm) and a red (650 nm) photoluminescence band in these samples will also be discussed.
- J-VIII/P32** EFFECT OF BF_2^+ IMPLANTATION ON THE STRAIN-RELAXATION OF PSEUDOMORPHIC METASTABLE $\text{Ge}_{0.06}\text{Si}_{0.94}$ ALLOY LAYERS, M.S. Oh, S. Im, and J.H. Song*, Department of Metallurgical Engineering, School of Materials Science and Engineering, Yonsei University, Seoul, 120-749, Korea; *Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, 130-650, Korea
For a doping method in strained GeSi thin films, in-situ method has mainly been used in growth chambers, because conventional implantation may accompany irradiation damage bringing enhanced relaxation of strain in the GeSi layers. Nonetheless, ion implantation doping was recently succeeded. In this study, we present dose-windows for successful strain-conservation, and the effects of BF_2^+ implantation on the strain-relaxation of pseudomorphic metastable $\text{Ge}_{0.06}\text{Si}_{0.94}$ alloy layers are discussed.
Metastable pseudomorphic $\text{Ge}_{0.06}\text{Si}_{0.94}$ layers(n-type) grown by MBE on Si(100) were implanted at room temperature with 70 keV BF_2^+ ions to doses of 3×10^{13} , 1×10^{14} , and 2.5×10^{14} cm^{-2} . The samples were subsequently annealed in a vacuum or nitrogen furnace for 30 min at 700, 800, and 900 oC. Observed by MeV 4He channeling spectrometry, as-implanted samples always show much higher backscattering yields than post-annealed ones and particularly the GeSi implanted at a dose of 2.5×10^{14} BF_2^+ cm^{-2} seems to be amorphized from surface to a depth of about 150 nm. Crystalline degradation of post-annealed $\text{Ge}_{0.06}\text{Si}_{0.94}$ samples becomes pronounced as the dose increases, although the samples implanted at 3×10^{13} cm^{-2} do not visibly degrade after annealing. Since the crystalline degradation observed after annealing is regarded as a signal of strain-relaxation, strain-relaxation seems to be enhanced as the implantation dosage increases. It is thus concluded that such a low dose of 3×10^{13} cm^{-2} can only conserve intrinsic strain. For a detailed study of such a behavior of strain-relaxation enhanced by ion beam damages, cross-sectional TEM, x-ray rocking curve, and current leakage measurements will be discussed.

E-MRS'98 SPRING MEETING



SYMPOSIUM K

Carbon-based Materials for Microelectronics

Symposium Organizers

| | |
|---------------------|-------------------------------------|
| J. FINK | IFW Dresden, Dresden, Germany |
| J. ROBERTSON | Cambridge University, Cambridge, UK |
| E. KOHN | Universität Ulm, Ulm, Germany |
| D. WALTON | University of Sussex, Brighton, UK |

SYMPOSIUM K

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - Nano-Graphite, Fullerenes

Chairperson: M. Knupfer, Inst für Festkörper- und Werkstofforschung, Dresden, Germany

- K-I.1** 9:00-9:30 - Invited - **GIANT POLYCYCLIC AROMATIC HYDROCARBONS AS NANOSCOPIC GRAPHITE MODELS**, A.J. Berresheim, J.-D. Brand, C.G. Fouracre, S. Ito, M. Wehmeier, **K. Müllen**, Max-Planck-Institute für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
Conjugated or molecule-based molecular structures of spherical and tubular form, have attracted interest as molecular wires. Another class of carbon based structures comprises large discs prepared from polycyclic aromatic hydrocarbon (PAHs), such as 1 and 2. Our recent work has made available extremely large representatives of this class of compounds. The important aspects of our synthesis are the systematic control of size and shape and in spite of the very large rigid structure, their processability. This processability makes it possible to organize these giant disc structures into π -stacked columnar arrays and also to detect monomolecular adsorbate layers on surfaces. Ordered monolayers of PAHs on substrate surfaces are prepared by UHV-deposition and by physisorption from solution. Current-potential curves recorded for single disc-type molecules and a drastic increase of charge-carrier mobility as a result of supramolecular order in the discotic mesophase are outstanding physical results.
- K-I.2** 9:30-9:50 **ORGANIC PHOTOCONDUCTORS FOR XEROGRAPHY**, C. Schlebusch, J. Morenzin, B. Kessler, and W. Eberhardt, Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, 52425 Jülich, Germany
Organic photoconductors as TiO-phthalocyanine and H₂-phthalocyanine are among the most common photo-receptor materials for photoactive layers in laser printer drums. By adding C₆₀ as electron acceptor the charge generation rate can be enhanced. With XANES we investigate the effect of C₆₀ on the unoccupied electronic states of dispersions containing H₂-phthalocyanine as used in electrophotography. Comparison of those technical samples with model samples of evaporated C₆₀/H₂-phthalocyanine layers is done. Together with UPS measurements an insight into the interaction between the materials and into the energetics of the charge transfer process can be achieved.
- K-I.3** 9:50-10:10 **Gd-L_{III} EXAFS STUDY OF Gd@C₈₂** H. Giefers, F. Nessel, M. Strecker, G. Wortmann, Universität-GH Paderborn, FB Physik, 33095 Paderborn, Germany and Yu.S. Grushko, E.G. Alekseev, V.S. Kozlov, St. Petersburg Nuclear Physics Institute, Gatchina 188350, Russia
The location of endohedral R ions (R = lanthanides, Y, Sc) inside the C₈₂ cage and their dynamic behaviour are of actual interest [1,2,3]. We report on an EXAFS study of Gd@C₈₂ employing the Gd L_{III}-edge in the temperature range 10 K to 300 K. From an analysis of the EXAFS oscillations with various models we derive a Gd position which is nearly centered above a carbon hexagon with nearest and next nearest C neighbours distances around 2.50(3) Å and 2.92(5) Å, similar to the case of Y@C₈₂ [3]. From the temperature dependence of the second cumulant we derive as in the case of the octahedral sites in A₃C₆₀ systems [4] direct information on the static (disorder) and dynamic (temperature) variance of these distances and on the bonding strength of Gd³⁺ ion to the inner C₈₂ surface. We present a model which will explain the extremely small Mössbauer f-factor observed in a Gd-155 Mössbauer study of the same sample.
[1] W. Andreoni et al., in: Fullerenes and Fullerene Nanostructures (World Scientific, Singapore 1996), p. 205.
[2] M. Takata et al., Nature 377, 46 (1995) and Ref. 1, p. 155
[3] C.-H. Park et al., Chem. Phys. Lett. 213, 196 (1993).
[4] G. Nowitzke et al., Phys. Rev. B 54, 13230 (1996).- Work supported by the DFG Wo-209/10).
- K-I.4** 10:10-10:30 **VIBRATIONAL CHARACTERISATION OF THREE TM@C₈₂ ISOMERS**, M. Krause, P. Kuran, A. Bartl, L. Dunsch, Institut für Festkörper- und Werkstofforschung Dresden, Helmholtzstr. 20, 01171 Dresden, Germany
Three isomers of the metallofullerene Tm@C₈₂ were studied by Raman spectroscopy at room and liquid nitrogen temperature and by infrared spectroscopy at room temperature. A thulium metal-C₈₂ cage Raman vibration was detected around 117 cm⁻¹. Its frequency was only little affected by the kind of cage isomer but is characteristic for +2 electronic state of the included thulium ion. The different cage isomers could be clearly distinguished by fingerprint-like spectral differences in the range of the internal cage modes. These were most pronounced between 1550 and 1650 cm⁻¹. At liquid nitrogen temperature slightly increased Raman frequencies and smaller half widths were found. On the basis of the very complete set of observed we discuss symmetry properties of the C₈₂ cages of the three Tm@C₈₂ isomers.

10:30-11:00

BREAK

SESSION II - Fullerenes, Nanotubes

Chairperson: C. Dekker, Delft University and DIMES, Delft, The Netherlands

- K-II.1** 11:00-11:20 **C₆₀ THIN FILMS ON Ag(001) : AN STM STUDY**, E. Giudice, E. Magnano*, S. Rusponi, C. Boragno, G. Costantini and U. Valbusa, Centro di Fisica delle Superfici e Basse Temperature - CNR and INFN, Unita' di Genova, via Dodecaneso 33, 16146 Genova, Italy, *Laboratorio TASC-INFN, Padriciano 99, 34012 Trieste, Italy
The morphology of C₆₀ films deposited on a Ag(001) single crystal has been studied using an UHV-STM as function of the substrate temperature. At room temperature, and at the beginning of the growth process, the molecules decorate the descending steps, and only in a second stage form irregular islands. The C₆₀ molecules are arranged in a quasi-hexagonal c(6x4) structure, having the long axis along the <110> direction of the Ag surface. Due to the existence of two equivalent directions, the C₆₀ film presents different domains, separated by dislocation lines. In each domain, peculiar structures of bright C₆₀ molecules have been resolved. These structures are not due to geometric effects, but to non-homogeneous charge distributions and different chemical bonding with the Ag substrate, as shown by XPD preliminary results. At low temperature, C₆₀ fractal islands are created. No color contrast is resolved, indicating a different bound with the surface. Bright molecules appear only after annealing at about 300 K. Sometimes, linear chains of C₆₀ molecules are present on the surface, having a length of several thousands Angstrom. These chains are probably due to a long range intermolecular interaction.
- K-II.2** 11:20-11:40 **RELATIVE STABILITIES OF ISOMERIC CAGES: IPR-, NON-IPR-, PSEUDO-FULLERENES**, Z. Slania, X. Zhao and E. Osawa, Laboratories of Computational Chemistry & Fullerene Science, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan
It has been well evident that non-IPR structures and even structures containing rings other than pentagons and hexagons (i.e., pseudo- fullerenes) should be tested computationally for their stabilities. Moreover, temperature effects on stabilities should be respected accordingly. In the report we predict (surprising) relative stabilities of some non-IPR structures and of some quasi-fullerenes with four- and seven-membered rings. The computations are based on semiempirical, ab initio Hartree-Fock, and ab initio density functional theory methods in conjunction with statistical-mechanical techniques. The results indicate that the ground-state structure is frequently not the species most populated under fullerene-synthesis conditions. For example, the complete set of 86 isolated-pentagon-rule (IPR) structures of C₉₂ is described by the SAM1 quantum-chemical method, and their energetics is also checked by ab initio SCF computations (HF/3-21G, HF/4-31G). Relative concentrations of the structures were further computed using the isomeric partition function.
- K-II.3** 11:40-12:00 - Invited - **SHEETS, CONES & TUBES**, **T.W. Ebbesen**, ISIS, Louis Pasteur University, 4 rue B. Pascal, 67000 Strasbourg, France and NEC Research Institute, 4 Independence Way, Princeton NJ 08540, USA
Graphitic sheets and the structures that can be made from these, such as cones and tubes, give us opportunities to develop new materials where the electronic properties are tailored to suit specific needs. While much progress has been made in this area over the last few years, some of the biggest challenges remain. This will be discussed together some of our most recent results.
- K-II.4** 12:10-12:30 - Invited - **DESIGN OF CARBON NANOSTRUCTURES TOWARD NEW MICROELECTRONICS**, **S. Saito**, Department of Physics, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan
Carbon is a unique element showing a variety of stable interatomic bondings with sp, sp², and sp³ hybridizations. Due to their flexible and resilient bonding nature, one can consider in principle the infinite number of carbon nanostructures with a great diversity of electronic properties. Combined with quantum-mechanical theoretical predictions, a macroscopic production of many kinds of fullerenes and carbon nanotubes during this decade has enabled us to explore this new fruitful field of great technological importance. I will report the electronic properties of carbon-nanotube materials studied in the framework of the density-functional theory and the quantitative tight-binding method. Also the quantum-mechanical material design of fullerene- and tube-based nanostructures including C₂₀ solids and pristine and doped crystalline tubes will be reported, and their interesting electronic and mechanical properties will be addressed from the viewpoint of the microelectronics.

12:30-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III - Nanotubes II**Chairperson: T.W. Ebbesen**, ISIS, Louis Pasteur University, Strasbourg, France

- K-III.1** 14:00-14:30 - Invited - CARBON NANOTUBES AS MOLECULAR QUANTUM WIRES, **C. Dekker**, Delft University of Technology, Department of Applied Physics and DIMES, Lorentzweg 1, 2628 CJ Delft, The Netherlands
- K-III.2** 14:30-14:50 PROCESSING OF SINGLE-WALL CARBON NANOTUBES FOR NANO-ELECTRONIC APPLICATION, **Y. Zhang**, S. Iijima, NEC, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan and E. Landree, Northwestern University, 2225 N. Campus Drive, Evanston IL 60208, USA
High-yield single-wall carbon nanotubes have been produced by pulsed laser ablation using the method similar to that by A. Thess et al. (Science, Vol. 273, p. 483, 1996). Electronic microscopic observation of the nanotubes indicated they formed very long and inter-connected bundles. The high elastic moduli of carbon nanotube bundles make them difficult to be processed by mechanical method. In the present work, we developed a new processing technique utilizing direct reaction of carbon nanotubes with silicon to form hetero-junctions and terminated bundles. The modified structures of single-wall carbon nanotubes were characterized by transmission electron microscopy. This technique is hopeful to be applied to fabricate nanotube-semiconductor hybrid devices and nano-scale field-emission devices
- K-III.3** 14:50-15:20 - Invited - ELECTRONIC STRUCTURE STUDIES OF UNDOPED AND POTASSIUM DOPED SINGLE WALL NANOTUBES, **M. Knupfer**, T. Pichler, M.S. Golden and J. Fink, Institut für Festkörper- und Werkstofforschung Dresden, 01171 Dresden, Germany; A. Rinzler and R.E. Smalley, CNST, Rice Quantum Institute, Rice University, Houston, Tx 77251, USA
We present momentum-dependent electron energy-loss measurements of bulk samples of purified pristine and intercalated single wall carbon nanotubes, in which both localized and delocalized electronic excitations can be identified. The dispersion of the π and the $\pi+\sigma$ plasmons are similar to those in graphite, signalling the graphitic nature of the electronic system along the tube axis. In contrast, the interband plasmons at low energy have a vanishingly small dispersion, and are related to transitions between the characteristic singularities in the density of states. Upon potassium intercalation the loss function exhibits a new, non-dispersive, plasmon at low energy, which could be related to the excitation of the charge carriers introduced upon intercalation.
- K-III.4** 15:20-15:40 ELECTRONIC PROPERTIES OF CHEMICALLY DOPED SINGLE WALL CARBON NANOTUBES, **P. Petit**, E. Jouguelet, C. Mathis, J.E. Fischer*, A.G. Rinzler** and R.E. Smalley**, Institut Charles Sadron, CNRS, 67083 Strasbourg, France; *LRSM, Univ. of Pennsylvania, Philadelphia 19104-6272, USA; **Center for Nanoscale Science and Technology, Rice Univ., Houston Texas 77251, USA
Unoriented bulk SWNT samples obtained by laser ablation have been shown to be metallic and to be easily doped by exposure to alkali or halogen vapours. In this communication, we present our results on chemically doped purified SWNT. The doping process consists in immersing the sample in a Naphthalen-Lithium radical-ion solution. Upon doping we observe a drop of the resistivity of more than one order of magnitude. Temperature dependent resistivity measurements and ESR experiments on undoped and doped bulk samples are compared. The doping process being performed by a chemical route, its reversibility as well as the possibility of controlling the doping rate, e.g. the density of states, will be discussed.

15:40-16:10

BREAK**SESSION IV - Nanotubes III, Applications****Chairperson: P. Petit**, Institut Charles Sadron, CNRS, Strasbourg, France

- K-IV.1** 16:10-16:30 SCANNING PROBE METHOD INVESTIGATION OF CARBON NANOTUBES PRODUCED BY HIGH ENERGY ION IRRADIATION OF GRAPHITE, **L.P. Biro***, G.I. Mark and J. Gyulai, Research Institute for Technical Physics and Materials Science, 1525 Budapest, POB. 49, Hungary; B. Szabo**, J. Kürti and N. Rozlosnik, Eötvös University, 1088, Puskin u. 5, Hungary; L. Frey and H. Ryssel, FhG-Institut für Integrierte Schaltungen IIS-B, 91058 Erlangen, Schottkystr. 10, Germany, * FUNDP, 5000 Namur, Rue de la Bruxelles 61, Belgium, ** Research Institute for Technical Physics & Materials Science, 1525 Budapest, POB. 49, Hungary
Most carbon nanotubes (CNT) are produced by one of the three methods; electric arc, laser ablation, or catalytic decomposition of a gaseous hydrocarbon. In every of these procedures, the CNTs are generated together with amorphous carbon. Therefore purification steps are needed to obtain pure nanotubes. We evidenced CNTs on graphite irradiated with low dose (10^{-12} cm⁻²), swift ($E > 100$ MeV), heavy (Ne, Kr, Xe) ions. Atomic force microscopy and scanning tunneling microscopy were applied to investigate the CNTs. It was found that the surface density of CNTs increases with the ion mass. In some cases CNTs were found which showed a regular vibration pattern when scanned with the AFM. In the case of Xe ions it was frequently found that the CNTs emerge from large area surface craters, which are attributed to surface sputtering by dense nuclear cascades, produced by higher order knocked on target atoms.

SYMPOSIUM K

K-IV.2 16:30-16:50

TECHNICAL AND ECONOMICAL FEASIBILITY OF CARBON NANOFIBER BASED H₂-STORAGE SYSTEMS, W. Schütz, H. Klos, Mannesmann Pilotentwicklung, Chiemgastr. 116, 81549 München, Germany; G. Reichenauer, P. Lamp, ZAE, Am Hubland, 97074 Würzburg, Germany; L. Jörissen, ZSW, Helmholtzstr. 8, 89081 Ulm, Germany; V. Trapp, SGL Technik GmbH, W.-v.-Siemens-Str. 18, 86405 Meitingen, Germany

Carbon nanostructured materials possess exceptional material properties like huge internal surface combined with high electrical conductivity. Physcial and chemical research results on hydrogen storage in carbon nanofibers will be presented. Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool in order to study hydrogen absorption in carbon nanostructures. In principal the NMR-spectroscopy is able to investigate the hydrogen storage capacity and mechanism. Some NMR-results will be discussed and compared with other physical investigation methods like gravimetric and volumetric hydrogen absorption measurements. These methodes are not able to clarify the absorption mechanism in contrast to the NMR-method.

Mannesmann company is very experienced in metalhydrid technology, especially in metalhydrid tank systems for hydrogen storage. Based on these former developments, we will present a concept for a H₂-storage system where Carbon NanoFibers (CNF) are used as storage medium. A H₂-sensor system will be introduced for monitoring the filling process, for example H₂ resistant temperature and pressure sensors.

A comparison of mass and volume of different tank systems will be discussed, which is used in conventional internal combustion engine vehicles and electrical vehicles based on fuel cells.

K-IV.3 16:50-17:10

ELECTRONIC AND FIELD EMISSION PROPERTIES OF CARBON NANOTUBES, J.C. Charlier, Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium

The electronic properties of carbon nanotubes, and especially the effect of the termination, were investigated within tight-binding and ab initio frameworks. As recently observed experimentally [1], sharp resonant valence band states, related to the tube ends, dominate the valence band edge and fill the bandgap. Our calculations performed on different tube topologies corroborate the presence of these sharp localised states which could strongly influence the field emission properties of the nanotube. The strength and position of such states with respect to the Fermi level depend sensitively on the relative positions of pentagonal rings in the hexagonal network and their degree of confinement at the nanotube end. Field emission microscopy experiments were carried out on single-wall nanotube films [2] and compared to the local electronic densities of charge associated to different tip states obtained from ab initio calculations. This research illustrates that single-wall carbon nanotubes might constitute well defined tips with perfect atomic structure for scanning probe microscopy.

[1] D.L. Carroll, P. Redlich, P.M. Ajayan, J.-C. Charlier, X. Blase, A. De Vita and R. Car, Phys. Rev. Lett. 78, 2811 (1997).

[2] J.-M. Bonard, T. Stöckli, W.A. de Heer, A. Châtelain, J.-C. Charlier, X. Blase, A. De Vita, R. Car, J. Salvétat and L. Forro, submitted for publication (1998)

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION V - Fieldemission

Chairperson: E. Kohn, University of Ulm, Germany

- K-V.1** 14:00-14:30 - Invited - **FIELD EMISSION DISPLAYS FROM DIAMOND LIKE CARBON, W.I. Milne and J. Robertson, Engineering Department, Cambridge University, Trumpington Street, Cambridge CB2 1PZ, UK**
Flat panel displays with a picture quality comparable to a cathode ray tube can, in principle, be obtained from field emission displays (FEDs). A typical FED uses the emission of electrons from a matrix addressed array of cathodes to excite phosphor pixels. Current FEDs use Spindt tip cathodes made from Mo, Si or W. The tips are necessary to provide the high fields required to extract electrons from such high electron affinity materials. An alternative is to use flat cathodes produced from low electron affinity materials. Recently diamond like carbon (DLC) has become an attractive candidate for this application. Although the basis of emission from metal surfaces is reasonably well understood little is known about the exact emission mechanism from the DLC films.
DLC can be deposited using several different techniques leading to a variety of different DLC types which can show markedly different field emission behaviour. In this paper we will present a review of field emission obtained thus far from the different types of DLC and discuss the possible emission mechanisms which have been forwarded over the last few years
- K-V.2** 14:30-15:00 - Invited - **FIELD EMISSION FROM DIAMOND, DIAMOND-LIKE AND NANOSTRUCTURED CARBON FILMS, O.M. Küttel, O. Gröning, L. Nilsson, and L. Schlappbach, University of Fribourg, Physics Department, Pérolles, 1700 Fribourg, Switzerland**
We have performed energy resolved electron field emission (FEED) on differently prepared carbon samples: CVD diamond, amorphous carbon and nanotube films emitting below 10 V/ μm . From a fit of the FEED data we can independently determine the workfunction as well as the field enhancement factor β at the emission site. In addition, these measurements allow one to exactly locate in energy the origin of the emitted electrons. On all the samples analysed so far, we measured emission from the Fermi level with a workfunction around 5 eV. Hence, the emission site is at the potential of the back contact and the physical mechanism is very well described by the field emission model, developed for metals.
In a model experiment we could show that possible energy shifts to lower kinetic energies in the FEED spectra can easily be explained by an ohmic loss across a surface resistance. In this experiment we studied field emission from a metallic μm sized cluster sitting on single crystal hydrogen saturated N-doped diamond. Shifts in the order of 2/3 of the applied potential could be observed due to the high surface resistance. Even though the diamond surface showed negative electron affinity (NEA), it can not explain the observed emission. NEA is very often mentioned when describing field emission from carbon films by an injection model. However, our measurements clearly show that the shifts in the FEED spectra are due to ohmic losses at the surface.
FEED measurements on nanotube films allow us to determine the workfunction to 5 eV and the local fields at the apex to 2500 V/ μm . These films emit well below 1 V/ μm . -The emitted electrons originate from continuum states at the Fermi level.
- K-V.3** 15:00-15:20 **FIELD EMISSION OF NITROGENATED AMORPHOUS CARBON FILMS, U. Hoffmann, A. Weber and C.-P. Klages, Fraunhofer-Institute for Surface and Thin Film Technology, Bienroder Weg 54e, 38108 Braunschweig, Germany**
Field emitter films based on nitrogenated amorphous carbon (a-C:N) were deposited by sputtering of graphite employing an electron cyclotron resonance plasma as argon and nitrogen ion source. To investigate the vacuum electronic properties the a-C:N films were deposited on chromium pattern on glass. Different types of pattern were used. In an UHV chamber the vacuum electronic properties of the films were checked by U/I and Fowler-Nordheim plots. To localize the emission sites the excitation of a low voltage phosphor (ZnO:Zn) was monitored by an CCD camera. After an activation by a vacuum arc discharge at macroscopic field of 8V/ μm , emission of electrons occurred at electrical fields as low as 3.2 V/ μm and current densities up to 1.4 mA/mm² were achieved at a macroscopic field of 6.7 V/ μm . The film resistivity of the a-C:N films was in the range of 0.1 - 1 ohm cm. The nitrogen content varied between 0.3 and 15 at.%. As revealed by nanoindentation measurements the microhardness was 11-19 GPa indicating a relatively low sp³ content. The a-C films were further investigated by SIMS, EPMA, XRD, SEM, AFM, and TEM to obtain informations about the film composition and morphology. The influence of film thickness, substrate bias and emitter geometry on the field emission was also surveyed.
- K-V.4** 15:20-15:40 **MODEL FOR EMISSION FROM DIAMOND AND DIAMOND-LIKE CARBON, J. Robertson, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK**
There is great interest in the electron field emission from diamond-like carbon (DLC) and diamond and their use as thin film cathodes in Field Emission Displays. The field emission in these systems shows many similar characteristics such as Fowler-Nordheim plots of their emission currents indicating either a very low emission barrier or a large field enhancement. Diamond is well known to have a low or negative electron affinity, but this is not so for DLC. It is also difficult to attribute field enhancement only to geometric effects as DLC has ultra-smooth surfaces. We propose a model based on the observation that different surface terminations (C-H, bare or C-O) of diamond can swing the surface band energies by over 2 eV. Thus, heterogeneous surface terminations will create strong surface band fluctuations, which screened out by the high defect densities over depletion distances of 10 nm produces local fields of order 1000 MV/m. These are the magnitude of the fields needed to account for the observed Fowler-Nordheim plots and electron emission energy distributions.

15:40-16:10

BREAK

SESSION VI : POSTER SESSION

16:10-18:30

See programme of this poster session p. K-11 to K-16.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

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SESSION VII - Diamond-Like Carbon

Chairperson: J. Robertson, Engineering Dept, Cambridge University, UK

K-VII.1 8:30-9:00

- Invited -

DIAMOND-LIKE CARBON AS A PASSIVATION LAYER IN HIGH VOLTAGE SEMICONDUCTOR DEVICES, G.A.J. Amaratunga, Dept. of Electrical Engineering and Electronics, University of Liverpool, Liverpool L69 3GJ, UK

Si power semiconductor devices are currently used for controlling currents of up to 5kA. In the off state, these devices have to be capable of withstanding voltages of up to 6kV at temperatures of 125°C without breaking down. The common method to support high off-state voltages is to have specially designed p-n junctions as part of the devices structure which are reverse biased in the off state. The high voltage is supported across depletion regions formed by the reverse biased junction. These depletion regions can be as large as 500µm. While the performance of high voltage p-n junctions in the interior of the Si wafer can be adequately controlled, there are significant problems in designing the termination of the junctions at the Si surface. One of the key problems is the loss of voltage drop across a depletion layer at the surface due charge accumulation in the protective surface insulating layer (typically silicon dioxide). One of the main causes for such charge build up is thought to be atmospheric humidity.

As a dielectric, diamond-like carbon (DLC) can exhibit properties of high resistivity (100 Mohm-cm) and breakdown voltage (10MV/cm) similar to diamond. It is therefore a candidate thin film material for placing on the surface high voltage Si power devices. Additionally it can also act as a very effective moisture barrier. Results from tests carried out on 4.5kV Si diodes and 1.2kV IGBT devices with DLC passivation are reported. The performance of hydrogenated, nitrogenated and highly diamond-like tetrahedral amorphous carbon films are discussed. These results are compared with other in the literature to gain some measure of the overall potential for DLC as a passivating material in high voltage power semiconductor devices.

K-VII.2 9:00-9:20

INSIGHTS ON THE DEPOSITION MECHANISM OF SPUTTERED AMORPHOUS CARBON FILMS, S. Logothetidis, M. Gioti, P. Patsalas and C. Charitidis, Department of Physics, Aristotle University of Thessaloniki, 54006, Thessaloniki, Greece

Low energy ion bombardment during growth of amorphous carbon (a-C) films deposited on Si, results to dense films, rich in sp³ C-C bonds which exhibit high hardness, elastic modulus and compressive stress. We present a detailed study of the growth mechanisms of a-C films deposited by rf magnetron sputtering under negative bias voltage (or Ar⁺ ion bombardment) in terms of their composition, density, optical and mechanical properties. The optical properties and the composition were studied by in-situ spectroscopic ellipsometry while X-ray reflectivity was used to study their density and surface morphology. The combination of these two techniques provide the kinetic of the film growth and a self consistent "checking" for the formation of a new amorphous carbon phase. The internal stresses were measured by the cantilever laser beam technique. The hardness and elastic modulus of the films were examined using both conventional depth-sensing indentation and continuous stiffness measurements nanoindentation techniques. The experimental results showed that stress and hardness are directly related with the sp³ C-C bonding in the film and described well with the so far proposed models on the formation mechanism of tetrahedral carbon. However, the film density, that is a composite property, was found to depend not only on the sp² and sp³ configurations but also on the new dense carbon phase and the SiC phases formed at the initial stages of growth.

K-VII.3 9:20-9:40

SYNTHESIS AND CHARACTERISTICS OF UNDOPED AND DOPED HIGHLY TETRAHEDRAL AMORPHOUS CARBON FILMS, Aixiang Wei, Shaoqi Peng, Department of Physics, Zhongshan University, Guangzhou, China; Dihui Chen, Ning Ke, W.Y. Cheung, S.P. Wong, Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Undoped and doped highly tetrahedral amorphous carbon (ta-C) films have been formed by magnetic filtered plasma stream in an Ar, Ar and N₂ mixture ambient, respectively. The optical and electrical properties of these films as a function of the substrate bias voltage V_b and nitrogen partial pressure P_N have been studied using UV-visible optical absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and electrical conductivity measurement in a temperature range from 300 to 500K. The results show that ta-C films with high sp³ fraction were formed when the substrate bias voltage V_b was in the range from -10 to -50V. The optical band gap of such ta-C films was found to be larger than 3eV. The films deposited at low P_N (<17%) are doped ta-C films, resulting in slightly drop of band gap and increase of room-temperature electrical conductivity. For sample deposited at P_N ≥ 50%, nitrogenation of films is very pronounced. The films have a wide band gap of 4.05 eV and extremely low conductivity. These suggest that a carbon nitride films is formed. The configurations of N atoms in ta-C network are identified and discussed.

K-VII.4 9:40-10:00

MICROSTRUCTURE OF POLYMER-LIKE HYDROGENATED AMORPHOUS CARBON INVESTIGATED BY IN-SITU INFRARED ELLIPSOMETRY, T. Heitz, B. Drévilion, C. Godet, J.E. Bourée, LPICM (CNRS), Ecole Polytechnique, 91128 Palaiseau, France

Polymer-like (PLC) hydrogenated amorphous carbon (a-C:H) films show intense room temperature photoluminescence in the visible range and can thus be used in electroluminescent displays [M. Yoshimi et al., Optoelectronics 7 (1992) 69]. Optical and PL properties (i.e. localised π states) are strongly related to the microstructure which remains poorly understood. PLC films were grown in a microwave-assisted RF plasma reactor. Increasing RF power leads to a higher number of structural units containing C=C bonds. Frequencies, widths and intensities of both bending and stretching C-H vibrations have been studied by in situ IR ellipsometry as a function of film thickness. As a new result, the sp² CH_n bending mode at 1405cm⁻¹ has been evidenced in the bulk of a-C:H, even in PLC films with higher bandgap. The RF power dependence of sp² CH_n intensity has been aromatic configurations. Since the oscillator strength of C-H vibrations is very sensitive to local environment (i.e. nature of the second neighbour C-C bond), the sp³ CH₃ bending modes have been investigated in detail. The ratio (I_g/I_{as}) of symmetric (1375 cm⁻¹) and asymmetric (1465 cm⁻¹) vibrations has been found to increase significantly as function of RF power. The latter behaviour shows that the nearest environment of methyl groups evolves with RF power from basically single bonds towards a mixture of single and double bonds, in quantitative agreement with organic chemistry data.

SYMPOSIUM K

K-VII.5 10:00-10:20

A STUDY OF THE EFFECTS OF NITROGEN INCORPORATION AND ANNEALING ON THE ELECTRICAL PROPERTIES OF HYDROGENATED AMORPHOUS CARBON FILMS, R.U.A. Khan, A.P. Burden, S.R.P. Silva, J.M. Shannon, and B.J. Sealy, School of Electronic Engineering, Information Technology and Mathematics, University of Surrey, Guildford, Surrey, GU2 5XH, UK

We have investigated the electronic properties of hydrogenated amorphous carbon films deposited using a Plasma Technology DP800 radio frequency plasma-enhanced chemical vapour deposition system. The deposition chamber is configured with a driven upper-electrode and an earthed substrate table. Films deposited on the driven electrode have an E_{04} optical band-gap of 1-1.5 eV and a refractive index of 2-2.5, and are hard and diamond-like. However, films deposited on the earthed electrode are softer and polymeric with an E_{04} optical band-gap of 3-4 eV and a refractive index of 1.5-1.7. Both types of film have been grown with varying amounts of nitrogen in an attempt to electronically dope them. Metal-insulator-metal (MIM) structures have been examined in order to assess the electronic conduction mechanism. Films grown on the driven electrode possess current versus voltage (I/V) characteristics which suggest Poole-Frenkel type conduction. However, the I/V characteristics of the films grown on the earthed electrode exhibit high resistivity (typically 10^{14} - 10^{15} Ω cm) and a large hysteresis possibly caused by charging of gap states.

In order to improve the properties of both the material and the contacts, we have studied the effects of annealing the devices. Parameters investigated include the annealing duration and temperature of both nitrogenated and non-nitrogenated films as a function of the I/V characteristics. This has been correlated with a study of the variation of E_{04} optical band gap, refractive index and thickness. Early indications suggest that annealing the samples grown on the earthed electrode to 400°C results in significant reductions in both resistivity (to $\sim 10^{10}$ Ω cm, similar to that of the unannealed driven electrode grown films), and hysteresis. Films containing nitrogen have been found to be more sensitive to annealing.

10:20-10:50

BREAK

SESSION VIII - Diamond I

Chairperson: G.A.J. Amaratunga, University of Liverpool, UK

K-VIII.1 10:50-11:20 - Invited -

GROWTH OF ELECTRONIC GRADE DIAMOND FILMS AND ITS APPLICATION, A. Flöter, DB Forschungszentrum, Ulm, Germany

K-VIII.2 11:20-11:40

RF-BIAS ENHANCED NUCLEATION AND ORIENTED GROWTH OF CVD-DIAMOND, P. Mangang, R. Locher, C. Wild, P. Koidl, Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastraße 72, 79108 Freiburg, Germany

We report on a new type of tubular microwave CVD-reactor which allows the diamond deposition on 2" diameter substrates. A RF-bias in addition to the microwave plasma can be applied. The potential between plasma and substrate can thus be adjusted resulting in a continuous ion-bombardment of even electrically insulating substrates. The reactor is equipped with a substrate heating for temperature control independent of the microwave power. *In situ* laser-interferometry is used for growth monitoring.

Applying the RF-bias in addition to the microwave plasma, we succeeded in diamond nucleation on silicon, sapphire and silica. Furthermore, it was possible to grow diamond films epitaxially on silicon. From x-ray rocking curve measurements, half-widths of the angular spread of the crystal orientation of 2.6° were determined.

In order to find a new pretreatment for diamond nucleation, we exposed several substrates to the RF discharge only. Subsequently <100> textured CVD-diamond growth was performed. Using this technique, oriented diamond growth was established on silicon, β -SiC, sapphire and silica. The Diamond nucleation density appeared to depend critically on the pretreatment parameters during the RF discharge. Therefore the nucleation density on silicon was determined in dependence of the various process parameters. X-ray polefigure measurements of diamond films on RF pretreated silicon substrates showed epitaxial diamond growth with a superimposed weak fibre texture component that increased with continuing RF pretreatment time.

K-VIII.3 11:40-12:10 - Invited -

DOPING OF DIAMOND, R. Kalish, Physics Dept. and Solid State Institute, Technion, Haifa 32000, Israel

The exceptional physical, electrical and chemical properties of diamond make it a most suitable material for the realization of unique electronic devices and for electrochemical applications which require chemically inert electrodes. Both these, however, require the diamond to be electrically conductive. Diamond, which under normal conditions is highly insulating, can be made conductive by doping. Boron doped, p-type diamond, is well established; it exists in nature, and can also be synthesized both during CVD diamond growth and by ion-implantation. In contrast, n-type diamond has, until recently, not been found, although several theoretical predictions and some experimental attempts to achieve it have been published.

The present paper reviews the status of doping diamond, emphasizing the most recent results on phosphorus doped n-type diamond. Some applications of doped diamond will also be mentioned.

K-VIII.4 12:10-12:30

δ -DOPING IN DIAMOND, M. Kunze, A. Vescan, P. Gluche, W. Ebert, and E. Kohn, Department of Electron Devices and Circuits, University of Ulm, 89069 Ulm, Germany

To overcome the well known limitations of diamond based devices due to the high activation energy of the boron acceptor (370meV at low doping level) δ -boron-doped homoepitaxial diamond films grown by microwave CVD were optimized an applied to field effect transistor structures. δ -or pulse-doped layer structures with peak-concentration above 10^{19} cm^{-3} have been proposed to reduce the activation energy however with a limited sheet doping concentration. Various electrical and physical measurements were used to obtain steep doping profiles and suitable FET channels (e.g. a sheet concentration of 1×10^{13} cm^{-2} at 1×10^{20} cm^{-3} peak concentration requires 1nm thin films). nitrogen incorporated in diamond layers leads to insulating films due to the high activation energy of 1.7 eV, but nevertheless it still acts as deep donor. Therefore, parasitic boron-doping tails could be cut by the use of nitrogen to obtain the required steep doping profiles. As one result we will present a novel lossy dielectric Junction FET channel with reduced activation energy and residual doping in the gate control layer compensated using nitrogen leading to high drain current densities of 20mA/mm at 20 μ m gate length and moderate operation temperatures of 200°C.

12:30-14:00

LUNCH

Thursday June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-Midi

SESSION IX - Diamond II

Chairperson: R. Kalish, Technion, Haifa, Israel

- K- IX.1** 14:00-14:30 - Invited - **ELECTRONIC PROPERTIES OF DIAMOND SURFACES, L. Ley**, Inst. f. Technische Physik, Universität Erlangen, Erwin-Rommel-Str. 1, 91058 Erlangen, Germany
There are at least two applications where the surface properties of diamond supposedly play a crucial role: the use of diamond in cold cathode emitters and the surface MESFET. I shall review some key surface electronic parameters such as band bending, surface Fermi level position, and electron affinity and how they relate to the structure, hydrogen coverage, and the graphitisation of single crystal diamond surfaces as they are taken through annealing temperatures up to 1200°C. By combining high resolution C1s core level spectroscopy and contact potential difference measurements with photoelectron yield spectra the first experimental values for electron affinities <0 will be presented for the (111) and (100) surfaces of diamond. Transition temperatures of surface phases are given with an accuracy of $\pm 10\text{K}$ using the phonon line position of diamond as a thermometer.
- K- IX.2** 14:30-14:50 **MECHANISMS OF SURFACE CONDUCTIVITY IN THIN FILM DIAMOND: APPLICATION TO HIGH PERFORMANCE DEVICES, H.J. Looi, L.Y.S. Pang, A. Molloy*, F. Jones*, M.D. Whitfield, J.S. Foord* and R.B. Jackman**, Electronic and Electrical Engineering, University College London, Torrington Place, London W1CE 7JE, UK; *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK
We have recently shown that high performance, high power schottky diode and MESFET transistor devices can be fabricated on commercially accessible CVD diamond by utilising a p-type surface conduction layer arising from the effects of near surface hydrogen. The origin of this conduction effect has been controversial. We have used I-V, Hall effect, SIMS, Raman, UPS and XPS to determine the nature and characteristics of this layer in a range of CVD diamond films. Our results indicate that the direct formation of acceptor states by hydrogen residing in the near surface of the film is the origin of the p-type carriers present rather than surface band bending effects. We are able to control the carrier density in this surface layer and have obtained carrier mobilities of up to $70\text{ cm}^2\text{Vs}^{-1}$ with interesting variations occurring between the different film types studied. We shall discuss our results in terms of the potential for engineering the surface hydrogen layer for use in high performance, room temperature diamond devices.
- K- IX.3** 14:50-15:10 **A LARGE RANGE OF BORON DOPING WITH LOW COMPENSATION RATIO FOR HOMOEPITAXIAL DIAMOND FILMS, J.P. Lagrange, A. Deneuille and E. Ghereart**, LEPES - CNRS, BP 166, 38 042 Grenoble Cedex 9, France
From its large band gap, high carriers mobilities, and very high thermal conductivity diamond appears well suited for a large number of applications, for instance power devices and high temperature electronics. Any device application requires the control of the doping level on a large range of concentration and a low compensation ratio for an efficient space charge zone. We show here, that both can be achieved by boron doping of homoepitaxial diamond films.
The epitaxial films are deposited by Microwave (2.45 GHz) Plasma CVD on Ib synthetic diamond crystals, at 820°C from 5 ppb to 80 ppm of diborane in 4% methane/ 96% hydrogen gas mixtures. The corresponding boron incorporation varies from 5×10^{16} to $8 \times 10^{20}\text{ cm}^{-3}$ in the diamond films from infrared absorption calibrated by SIMS. The room temperature resistivity varies from 10^5 to $10^{-3}\Omega\text{cm}$. The conductivity was measured from 100 to 1000°K which allows to determine the ionisation level and the compensation ratio of boron doping atoms, and the conduction process. Full ionisation above 600°K is obtained for the lower incorporation levels ($[B] < 10^{17}\text{ cm}^{-3}$), while a boron impurity band appears from $[B] = 5 \times 10^{18}\text{ cm}^{-3}$, and metallic conductivity from $[B] = 3 \times 10^{20}\text{ cm}^{-3}$. Fits at both low and high temperatures of the $\sigma(T)$ curves indicate a low level of compensation around 5% at $2 \times 10^{18}\text{ B-cm}^{-3}$, while a high level of RT hole mobility ($550\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ Hall effect) is still kept at these high doping level.
- K-IX.4** 15:10-15:30 **OPTIMISATION OF CVD DIAMOND GROWTH FOR RADIATION DETECTOR FABRICATION, R.D. Marshall, P. Bergonzo, F. Foulon; A. Brambilla, B. Guizard, LETI (CEA-Technologies Avancées)/DEIN/SPE, CEA/Saclay, 91191 Gif-sur-Yvette cedex, France**
Commercially available polycrystalline CVD diamond is finding increasing applications in micro-electronics owing to its combination of extreme material properties. Such properties are necessary for the realisation of advanced radiation detectors where low temperature-susceptibility, high radiation-hardness and resistance to corrosive media are essential. In most cases this material is grown on Si substrates using a diamond powder scratching stage to enhance nucleation. However, such a process can be detrimental to the ultimate electronic properties of any device using the Si as one contact electrode. In contrast, Bias Enhanced Nucleation (BEN) offers a controllable nucleation stage which, following identical growth conditions, is shown to have an influence on the resulting electronic properties of devices. We report a study of the alpha particle detection properties from scratch and bias nucleated diamond film and correlate the results with nucleation density and the electronic properties of the interface. We present the conditions necessary for maximising the area of epitaxially oriented nuclei and achieving a uniform nucleation density over a two inch wafer.
- 15:30-16:00 **BREAK**

SYMPOSIUM K

SESSION X - Diamond III

Chairperson: L. Ley, Electronic Properties of Diamond Surfaces, Erlangen, Germany

- K-X.1** 16:00-16:20 **MINORITY-CARRIER TRANSPORT PARAMETERS IN CVD DIAMOND**, S. Salvatori, M.C. Rossi, F. Galluzzi, Dip. Ingegneria Elettronica, Università di Roma Tre, v. Vasca Navale 84, 00146 Roma, Italy
A detailed study on minority carrier transport parameters in CVD diamond films with different morphology is presented. Minority carrier mobility-lifetime values are obtained by steady-state electric field dependence of photocurrent and by time-resolved photo-responses under pulsed light excitation, both yielding $\mu\tau$ products in the range 10^{-9} - 10^{-6} cm² V⁻¹; lower values are generally found in small grain randomly oriented films whereas higher values refer to large-grain textured materials. Such a difference mainly reflects variations in mobility values, while minority carrier lifetimes in the sub-nanosecond range, exhibit only a minor dependence on diamond structure. Possible reasons for such lifetime values are discussed and related to diamond gap state distributions, as obtained by comparing sub-gap photocurrent and photoluminescence spectra. Spatial distribution of scattering and recombination processes is also discussed, attempting to separate intragrain and grain-boundary contributions.
- K-X.2** 16:20-16:40 **HIGH PERFORMANCE DEVICES FROM SURFACE CONDUCTING THIN FILM DIAMOND**, H.J. Looi, M.D. Whitfield, J.S. Foord* and R.B. Jackman, Electronic and Electrical Engineering, University College London, Torrington Place, London W1CE 7JE, UK; *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK
Diamond offers the prospect of high performance electronic devices for power and sensing applications. However, early diodes and field effect (FET) transistor devices fabricated using conventional boron doped material exhibited poor performance at room temperature arising from a combination of the defective nature of CVD material and the relatively high activation energy (0.37 eV) of the boron dopant in the diamond lattice. Recent reports have shown that devices can be fabricated on single crystal diamond by utilising the p-type conductivity provoked by near surface hydrogen. In this paper we show that a similar layer can be created in the more commercially accessible CVD thin film form of diamond (which is polycrystalline) resulting in schottky diodes and metal-semiconductor FET's (MESFETS) which display excellent room-temperature characteristics; diodes with rectification ratios $> 10^6$, leakage current < 10 nA, no breakdown at 100V reverse bias and an ideality factor of 1.1 have been fabricated. Simple MESFET structures which show extremely high power handling, low leakage and good saturation (pinch-off) characteristics have also been made. Powers of > 10 W/mm should be realisable from these structures, significantly greater than the current state-of-the-art in, for example, SiC.
- K-X.3** 16:40-17:00 **ELECTRON ENERGY-LOSS SPECTROSCOPY IN TRANSMISSION ON UNDOPED AND DOPED DIAMOND THIN FILMS**, S. Waidmann, K. Bartsch, I. Endler, F. Fontaine*, B. Arnold, L. Sümchen**, M. Knupfer, A. Leonhardt and J. Fink, Institut für Festkörper- und Werkstofforschung Dresden, 01171 Dresden, Germany; *Forschungszentrum Rossendorf, 01314 Dresden, Germany; **Institut für Analytische Chemie, Technische Universität Dresden, 01062 Dresden, Germany
We have prepared diamond thin films by microwave chemical vapour deposition (MWCVD) and hot filament chemical vapour deposition (HFCVD). Diamond powder pretreatment of the silicon substrates or bias potential were used for nucleation enhancement. Doping of the films was achieved in two ways: In-situ during the CVD process or after the deposition by ion implantation. Scanning electron microscope (SEM), transmission electron microscope (TEM) and RAMAN investigations were carried out to characterize the films. Electron energy-loss spectroscopy in transmission is then used to investigate the electronic structure of the diamond films as a function of processing parameters and the doping level.
- K-X.4** 17:00-17:20 **COMPUTER SIMULATIONS OF IMPLANTATION DAMAGE IN DIAMOND AND ITS ANNEALING**, D. Saada, J. Adler and R. Kalish, Physics Department, Technion, Haifa 32000, Israel
Diamond is a metastable form of carbon in which the atoms are bonded by sp³ hybridization. The stable bonding configuration of C is in the sp² hybridization, which corresponds to graphite. These two configurations are separated by a potential barrier. Ion-impact in diamond breaks many diamond bonds and may thus create vacancies, interstitial or metastable bonds in either the sp² or sp³ hybridization. The formation of these broken bonds and their rearrangement upon heating are studied at the present work by molecular dynamics and Monte Carlo computer simulations, using the Tersoff potential. The validity of the calculations is verified by comparing the displacement energy to results of others. New information on the configuration of stable defects in damaged diamond and on the transformation that damaged diamond undergoes as a result of heating is obtained. It is found that upon annealing (at 3000K) some disrupted diamond bonds will reform as sp² bonded "graphitic" layers which are preferentially oriented in the $\langle 111 \rangle$ direction.
- K-X.5** 17:20-17:40 **PHOTOCONDUCTIVITY OF DIAMOND-LIKE CARBON**, A. Ilie, J. Robertson, N. Conway, B. Kleinsorge, W.I. Milne, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK
The photoconductivity in tetrahedrally bonded amorphous carbon (ta-C) and hydrogenated ta-C (ta-C:H) has been investigated as a function of temperature, light intensity and wavelength. Transport and recombination parameters are derived and they are compared and contrasted to those of a-Si:H. Ta-C(:H) are found to be low mobility solids with a $\mu\tau$ product of about 10^{-12} cm²/V. The photoconductivity has a sublinear dependence on light intensity over a wide temperature range and the temperature dependence becomes weak below room temperature. The photon energy was varied, to study the effect of exciting into the extended states at higher energy. This is the first thorough study of photoconductivity in diamond-like carbon.

END OF SYMPOSIUM K

SYMPOSIUM K

SYMPOSIUM K
POSTER SESSION

Wednesday June 17, 1998
Mercredi 17 juin 1998

Afternoon
Après-midi

Session VI : Poster Session
16:10-18:30

- K-VI/P1** **STRUCTURE, DYNAMICS AND OPTICAL PROPERTIES OF FULLERENES AND FULLERITES C_{60} AND C_{70} ,**
Y. Prylutsky, Dept. of Physics, Kyiv Shevchenko University, Volodymyrska Str. 64, 252033 Kyiv, Ukraine
The intermolecular vibrational spectra of C_{60} and C_{70} fullerenes are calculated using the simple force model. The quantitative and qualitative analysis of dynamic Jahn-Teller effect in C_{60} fullerene is performed.
The crystalline phase of C_{60} and C_{70} fullerenes is studied at low temperature in dependence on the external pressure by use of ab-initio molecular dynamics approach. The intermolecular vibrational spectra of solid C_{60} and C_{70} in the Brillouin zone centre, sound velocities and elastic constants are calculated taking into account the theoretical-group methods.
The direct one-phonon and Raman two-phonon relaxation processes in the photoexcited triplet states of C_{60} and C_{70} fullerene are investigated in dependence on the temperature, value and direction of magnetic field. The influence of dynamic Jahn-Teller effect in C_{60} fullerene on the value of spin-lattice relaxation time is discussed.
The comparison of obtained theoretical results with available experimental data is carried out.
- K-VI/P2** **DOPING MECHANISM IN ta-C, C.W. Chen, J. Robertson, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK**
Nitrogen and boron are known to act as weak substitutional dopants in highly sp^3 bonded forms of diamond-like carbon known as ta-C. As even these materials have considerable sp^2 sites, there are a wide range of possible configurations for a nitrogen site to occupy in ta-C. These have been classified as σ bonded or π bonded, and either doping or non-doping. It is also necessary to consider whether doping sites are accompanied by defect sites, as occurs in a-Si:H. We have calculated the total energy of these various sites. Non-doping sites are found to be generally the more stable, which accounts for the low doping efficiency. 4-fold N sites are found to be accompanied 5-fold sp^2 rings rather than dangling bonds. This accounts for the observation that doping does not degrade the luminescence efficiency in a-C:H, as it would in a-Si:H.
- K-VI/P3** **ELECTRON RECOMBINATION IN a-C:H, ta-C and ta-C, J. Robertson, Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK**
Hydrogenated amorphous carbon contains both sp^2 and sp^3 sites. We previously proposed that the sp^2 sites are arranged in clusters [1], but disorder opposes clustering, so the clusters are smaller than originally proposed. We developed a model of recombination and luminescence in a-C:H. We assume that electron-hole pairs are created within an sp^2 cluster and can only radiatively recombine within that cluster. Carriers which tunnel out of their cluster will ultimately recombine non-radiatively. Localized states extend over a complete cluster, so the radiative coupling matrix element is larger than in a-Si:H. This accounts for the faster luminescence in a-C:H. The localized states decay rapidly between clusters, so carrier tunneling is more difficult than in a-Si:H. The tunneling rate is related to the cluster density and, using experimental data, to the band gap. The model thereby accounts for the observed dependence of luminescence efficiency on band gap, rather than defect density [2].
[1] J. Robertson, Phys Rev B 53 16302 (1996)
[2] S. Schutte, S. Will, H. Mell, W. Fuhs, Diamond Related Mats 2 1360 (1993)
- K-VI/P4** **QUANTUM CONFINEMENT AND OPTICAL ABSORPTION OF DIAMOND-LIKE AMORPHOUS CARBON, P. Mpawenayo and A. Tagliaferro, Dipartimento di Fisica, Politecnico di Torino, corso duca degli Abruzzi 24, 10129 Torino, Italy**
A quantum confinement theory is applied for modelling the optical absorption in the diamond-like amorphous carbon. The sp^2 phase is treated as composed by isolated spherically shaped clusters whose radii are distributed in a Gaussian manner, embedded in the sp^3 bonded diamond phase. Exciton confinement in graphitic clusters is at the origin of the blue-shift in absorption at higher energies.
Transition energy values, between hole states and electron ($1s$) excitonic states, are calculated by utilizing the effective-mass method for the treatment of the confinement problem in zero dimension quantum wells.
The overall absorption coefficient is averaged in function of the volumetric ratio of sp^2 phase. Optical absorption peaks are located between 1.8eV and 3.2eV on optical absorption curves.
The unusual Tauc's optical gap and Urbach tail parameter are explained. It is shown that the model consisting in the description of the absorption coefficient of amorphous carbon as a product of gaussian and error functions is equivalent to the one band approximation that does not take into account the band splitting.
- K-VI/P5** **FORMATION OF A THICK C_{60}/C_{70} MEMBRANES, V.F. Masterov, A.V. Prikhodko, Exp. Phys. Depart., St. Petersburg State Technical University, 195251 St. Petersburg, Russia; O.I. Konkov, V.Yu. Davydov, Ioffe Physiko-Technical Institute, 194021 St. Petersburg, Russia**
We present an original method for growing large fullerene membranes. In a basis of a method lays thermal sublimation. This technique can produce high-quality polycrystalline C_{60} and C_{70} fullerene membranes with size up to some mm (diameter 2-8 mm and thickness up to 2.5 mm) which is the largest size reported up to now. The results of micro Raman measurements are presented and discussed. Membranes made of a fix C_{60}/C_{70} fullerenes have allowed to receive the spacial separation of various types of fullerenes in the same sample. On the top surface of a sample Raman lines, conterminous with the basic lines C_{60} are registered only, while on the bottom surface of the sample the maximum intensity have the lines, that specifies primary formation of C_{70} . Found out separation of fullerenes during formation of a membrane allows not only to receive "twin" C_{60}/C_{70} membranes, but also to supervise their phase structure by a choice of a target composition.
- K-VI/P6** **WITHDRAWN**

- K-VI/P7** CHROMIUM IN AMORPHOUS CARBON BASED THIN FILMS PREPARED IN A PACVD PROCESS, P. Gantenbein, S. Brunold, School of Engineering ITR, Oberseest. 10, 8640 Rapperswil, Switzerland
The deposition of Cr containing a-C:H thin films in a rf and mf PACVD process is described, a-C:H/Cr films were deposited on Si and Cu substrates. Negative dc bias voltage at the substrate and the composition of the process gas are two significant parameters in the deposition process. By applying a higher bias voltage the growth rate is increased. The dependence on the ratio of CH₄ to Ar shows a saturation effect in the region of high CH₄ concentration. This shows the significant contribution of an ion current to the film growth and a space charge limited ion current in the selected parameter range. A increase of the Cr content in the a-C:H films by increasing the CH₄ flow ratio is measured by XPS while a correlation of the density of the electronic states at the Fermi level with the metal content in the a-C:H matrix is observed by UPS. No significant change in the ratio of sp² to sp³ bonded carbon atoms in the films deposited with the two methods is observed by Raman spectroscopy. SEM is confirming the film model of electrical conducting regions embedded in a isolating matrix. The metallic regions are formed by the Cr₇C₃ phase and the matrix material consists of a-C:H. Optical reflectivity measurements at three layer films on Cu show there solar selectivity. Ageing tests of the samples at 250°C in air showed the increase of the solar absorption as well as the reduction of the thermal emission after 80 h treatment. These results show a total suppression of the cooper diffusion through the diffusion barrier in the three layer system.
- K-VI/P8** A STUDY OF ELECTRON INTERACTIONS IN FULLERENE DERIVATIVES, L.G. Bulusheva and A.V. Okotrub, Institute of Inorganic Chemistry SB RAS, av. Lavrenteva 3, 630090 Novosibirsk, Russia
Electronic structure of fullerene compounds C₆₀F₂₄, C₆₀H₃₆ and (C₆₀)_n was investigated by quantum-chemical and X-ray spectroscopy methods. We calculated the numbers of isomers of C₆₀F₂₄ and C₆₀H₃₆ and (C₆₀)₂, (C₆₀)₃ structures by semiempirical PM3 method. High resolution fluorescence CKα spectra of fluorofullerene, hydrofullerene and polymerized fullerene were measured on laboratory X-ray spectrometer. The theoretical spectra for each molecule were plotted in the Koopman's theorem framework. These spectra were correlated with experimental data and the preferable structures for investigated compounds were chose.
In C₆₀F₂₄, fluorine atoms were found to be situated by the belt around the C₆₀ molecule. The best agreement between experimental and theoretical data in the case of hydrofullerene was obtained for the T symmetry isomer, having four aromatic benzene ring in the tetrahedral positions. Theoretical CKα spectra were simulated for a polymeric chain, two-dimensional and three-dimensional polymer. Fullerene molecules were shown to have the coordination up 4 to 6 in amorphous polymerized material.
The structure of the electron interactions in these fullerene derivatives has been investigated in terms of the fragment analysis.
- K-VI/P9** X-RAY SPECTROSCOPIC CHARACTERIZATION OF CARBON-BASED MATERIALS, A.V. Okotrub, L.G. Bulusheva and L.N. Mazalov, Institute of Inorganic Chemistry SB RAS, av. Lavrenteva 3, 630090 Novosibirsk, Russia
The shape of CKα spectra depends on the carbon atoms states in the carbon-based materials. We use CKα fluorescent spectra for the investigation of structure particularities of ultra dispersed diamonds (UDD), fluorographites CF_x (x=0.5 - 1.33), fullerenes C₆₀, C₇₀ and carbon nanotubes. Spectra were measured on the laboratory X-ray spectrometer with resolution 0.5 eV. The interpretation of spectra were performed on the base of quantum-chemical calculations of various structure models by semiempirical method PM3.
Short-wave maxima of different intensity are observed in CKα spectra of UDD particles of the various size. Modeling of ratio of bulk and surface states of carbon atoms allows to determine the characteristic particle size. The CF/CF₂ ratio in the fluorographite samples was determined from the intensity of shoulder in CKα spectra and quantum-chemical simulation. CKα spectra of cage carbon materials are characteristic. We detected the distinguishes in the spectra of various fullerenes and carbon nanotubes produced in different synthetic conditions. Theoretical spectra of (n,0) tubes correspond to the experimental spectrum of the inner part of cathode deposit. CKα spectrum of the soot containing the single wall tubules is in the best agreement with the calculation of (n,n) nanotubes.
- K-VI/P10** SECOND HARMONIC GENERATION (SHG) SPECTROSCOPY OF FULLERENE LANGMUIR FILMS, O.A. Aktsipetrov, E.D. Mishina, T.V. Misuryaev, A.A. Nikulin, V.R. Novak, Department of Physics, Moscow State University, Moscow 119899, Russia, and Th. Rasing, Research Institute for Materials, University of Nijmegen, Nijmegen, The Netherlands
Fullerene molecules possess high values of nonlinear optical (magneto-dipole) hyperpolarizabilities in spite of their inversion symmetry. Thin films of controlled thickness with monolayer resolution and molecular ordering within the layer can be fabricated using the Langmuir-Blodgett technique. Second Harmonic Generation provides a reliable diagnostic tool for such films. To obtain mono-molecular fullerene layers a modification of C₆₀ molecules by amphiphilic organic groups is required. Besides, modification breaks an inversion symmetry of C₆₀ molecules that should give rise to a dipole hyperpolarizability, that is generally higher in comparison with a magneto-dipole one. We show here, however, that depending on the nature of organic group, the modification of C₆₀ molecules can both increase and decrease the SHG intensity in thin fullerene films. This can be explained in terms of individual polarizability, although the difference in molecular packing should be taken into account as well.
- K-VI/P11** FRENKEL EXCITATIONS OF CN (N=12,60) CLUSTERS, S.V. Rotkin, Ioffe PTI, Polytechnicheskaya 26, 194021 St-Petersburg, Russia
The problem of Coulomb interaction between charge carriers in carbon clusters has been attacked successfully within the mean-field approach [1], and by the restriction of the relevant state space [2]. In contrast to previously considered doped fullerene system we solved the exciton problem in pristine C₆₀ and C₁₂ clusters. The lattice group of the later being truncated tetrahedron (C₆₀ is truncated icosahedron) is much simpler for analysis though belongs to the same triangular lattices. The SO(4) supersymmetry is speculated to be useful for the C₁₂ state classification. The projections onto SO(3) and the lowermost tetrahedral group spaces are presented. The application of the same method to C₆₀ is discussed. It is well-understood that the intercluster hopping in condensed fullerene is negligible, though dipole-dipole intercluster interaction is weak due to the low substance density and will not be discussed here. So far the exciton is localized on the single cluster. We propose the simple model reflecting the actual cluster symmetry as well as the symmetry of reduced two-particle Hamiltonian. The simplification results from the supposition that the only electron-hole state is to be included in the calculation. We show that multipole decomposition of the Hubbard model in this case leads to the Frenkel-like Hamiltonian which spectrum can be derived analytically using standard group theoretical technique.
[1] M. Rasetti et al., Phys. A199, 539, 1993. [2a] A. Auerbach et al., Phys. Rev. Lett. 72, 2931, 1994. [2b] R. Friedberg et al., Phys. Rev. B46, 14150, 1992.
- K-VI/P12** THE NANOSECOND ELECTRIC TRANSPORT IN Cu_nC₆₀ COMPOUNDS (POWDER AND FILMS), V.F. Masterov, A.V. Prikhodko, Experimental Phys. Depart., St. Petersburg State Technical University, 195251 St. Petersburg, Russia and O.I. Konkov, Ioffe Physiko-Technical Institute, St. Petersburg, Russia
We have previously reported the observation of a superconducting phase transition in powder samples of Cu_nC₆₀ at temperatures of 80-120K. We have subsequently confirmed this conclusion by SQUID, magnetic susceptibility and microwave absorption experiments. Here we report an investigation of electrical characteristics of powdered samples and thin films of Cu_nC₆₀ by nanosecond VAcH. This method is capable of minimizing the heating of weak spots in the sample. The powdered samples were prepared from C₆₀ and electrolytic copper, which were mixed in the ratio 7.5:1 to establish a stoichiometric Cu_{1.5}C₆₀ composition. The films were prepared by thermal evaporation of copper and simultaneous sublimation of C₆₀. The samples were subjected to x-ray microanalysis, x-ray structural analysis and IR-spectroscopy. A procedure based on the recording of pulses incident on and reflected from the sample was used for measurements in the nanosecond range of pulse duration (0.5-10 ns). The results of this study confirm the existence of a phase transition at 90K in the powdered Cu_nC₆₀ samples, its occurrence depending on the number of thermal cycles in the range 80-150K. A similar effect is also observed in thin films of similar composition (Cu_{1.2-1.8}C₆₀), where the thermal cycles result in a variation of the T_c from 83 to 103K.

- K-VI/P13** LASER ABLATION PLASMA DEPOSITION OF CLUSTER-ASSEMBLED CARBON POWDERS, V.S. Burakov, A.F. Bokhonov, V.L. Kasyutich, N.A. Savastenko, M.I. Nedel'ko, and N.V. Tarasenko, Institute of Molecular and Atomic Physics National Academy of Sciences, 70 Scaryna Ave., 220072 Minsk, Belarus

Pulsed laser ablation plasma deposition technique for fabrication of cluster-assembled carbon powders was applied with characterization of ablated plasma by laser-induced fluorescence and time-resolved optical emission spectroscopy. Analysis of the deposited material was accomplished by non-aqueous capillary electrophoresis with laser refractive index detection. The Nd-YAG (1064nm, 10ns, 100mJ) and excimer XeCl (308 nm, 10 ns, 5mJ) lasers were employed for ablation of graphite target placed in the chamber with helium atmosphere at pressures varying in the range 0.1 - 400 Torr. The power densities on the target surface was 10^8 - 10^9 W/cm². The time-space distributions of C₂ and C₃ molecules as well as the vibrational temperature of C₂ molecules in the ablated plasma were obtained. The results indicated that the dominant mechanism for production of C₂ was the atomic carbon recombination. Considering the presence of these molecules in plasma as a first step in the formation of large carbon clusters the correlation of this process with initial conditions of plasma creation (laser intensity, pressure of the surrounding gas) was established. The correlation obtained was supported by results of separation of carbon clusters from the deposited material using the adopted capillary electrophoresis method.

- K-VI/P14** CARBON ONION INTERSHELL ORIENTATIONAL MELTING, Yu.E. Lozovik, A.M. Popov, Institute of Spectroscopy, Russian Academy of Science 142092, Troitsk, Moscow region, Russia

The possibility of intershell orientational melting of two-shell carbon nanoparticle with fullerene C₆₀ as inner shell and fullerene C₂₄₀ with icosahedral symmetry as outer shell is considered.

The global and local minima of total potential energy of nanoparticle are found by optimization of three angles of relative shell orientation. The high I_h symmetry of shells leads to great number of equivalent global minima. The energies of shell deformation are also calculated. The barriers for relative rotation of shells in nanoparticle under consideration are calculated. It is found that the obtained values of barriers for rotation are surprisingly small and shell deformation during intershell rotation does not considerably influence on the magnitudes of barriers.

The temperature T₁ of crossover from frozen state of nanoparticle to jump rotational intershell diffusion of shells is estimated to be several Kelvin degrees. The temperatures T₂ of crossover from jump rotational diffusion to free rotation of shell is identified as the point where the two free energies of these states are equal. These temperatures are about tens Kelvin degrees. Both temperatures T₁ and T₂ are determined by the shape of second shell.

The molecular dynamics simulation of the process of nanoparticle orientational melting is performed.

- K-VI/P15** BORON ION-IMPLANTATION IN DIAMOND: STATE OF THE ART, C. Uzan-Saguy, V. Richter, B. Ran and R. Kalish, Physics Dept. and Solid State Institute, Technion, Haifa 32000, Israel

P-type diamond can be achieved by boron ion-implantation followed by annealing. Several implantation schemes have been proposed over the years, differing in implantation conditions and in post-growth annealing procedures.

In the present work we report on a systematic study of different implantation/annealing schemes and their effectiveness in obtaining high doping efficiencies and hole mobilities. Different implantation temperatures (from 77K to 1300K) were employed and both rapid thermal annealing and high temperature furnace annealings were performed. The effectiveness of these was determined from temperature dependent Hall effect measurements.

- K-VI/P16** EVALUATION OF VARIOUS REACTIONS APPLIED TO PRODUCE C₆₀Fe COMPOUND, E. Kowalska, P. Byszewski*, J. Radomska, R. Diduszko, Institute of Vacuum Technology, Długa 44/50, 00-241 Warsaw, Poland (*also at Institute of Physics PAS, al.Lotnikow 32/46, 02-668 Warsaw); Z. Kucharski, Institute of Atomic Energy, 05-400 Swierk, Poland; A. Huczko, H. Lange, Department of Chemistry, Warsaw University, L. Pasteura 1, 02-093 Warsaw, Poland; R. Kochkanjan, Institute of Physico-Organic and Coal Chemistry NAS, R. Luxembourg 68, 340-114 Donetsk, Ukraine; V. Chabanenko, Physico-Technical Institute NAS, R. Luxembourg 72, 340-114, Donetsk, Ukraine

Using ferrocene as a source of iron, we prepared fulleride samples with iron dissolved in the fullerene based lattice. The procedure consisted of three steps: 1, modification of ferrocene to weaken iron bonding to the ligands; 2, extraction of iron from the weakened ferrocene derivative and binding it to fullerene; 3, removing of residual organic groups from the dried solid. The first step can be achieved by polymerizing or by substituting one of cyclopentadienes of ferrocene by solvate under the influence of catalyst (nitric acid or aluminiumtrichloride). The reaction with fullerenes begins in toluene or benzene solution and proceeds further when the solution is dried. The samples prepared by those methods were analyzed by mass spectrometry, thermal analyses, X-ray diffraction and Mössbauer spectroscopy methods. We detected in these sample iron in the ionization state either +2 or +3 depending on thermal treatment of the samples but not any iron clusters.

- K-VI/P17** EXPERIMENTAL ELECTRONIC STRUCTURE STUDIES OF INTERCALATED, HETERO AND ENDOHEDRAL FULLERENES, S. Waidmann, M. Knapfer, R. Friedlein, T. Pichler, M.S. Golden and J. Fink, Institut für Festkörper- und Werkstofforschung Dresden, 01171 Dresden, Germany

There are three possible ways to selectively alter the charge on fullerene molecules in a solid: doping via intercalation, on-ball doping via substitution of C-atoms with heteroatoms and endohedral doping by inserting a metal ion inside the carbon cage. We present recent experimental results on the electronic structure of fullerenes doped using each of these strategies, which have been obtained using photoemission spectroscopy (PES) and electron energy-loss spectroscopy (EELS) in transmission. In detail, the ground state of A₄C₆₀ materials, the valence band electronic structure of undoped and alkali metal intercalated (C₅₉N)₂ and the valence state of Tm in Tm@C₈₂ will be discussed.

- K-VI/P18** FIELD EMISSION OF ELECTRONS FROM CARBON CLUSTERS C₆₀, A.A. Paiziev, Laboratory of Positron Diagnostics Institute of Electronics Uzbek Academy of Sciences, Akademgorodok, 700143 Tashkent, Uzbekistan

At present the complete understanding in problem of electron field emission from carbon clusters C-60 is absent. This problem is acquiring significant actuality connected with perspective using of carbon nanotubes as effective electron emitters.

In present work new understanding about electron structure of the carbon clusters C-60 is described. It is suggested that valent electrons which are forming the double bond in the fullerene molecules form the conductive spherical layer with radius equal to radius of the fullerenes. In the framework of this model the energetic spectra and wave functions of the conductive electrons have been calculated. In quasiclassical approach a probability of the electron emission from carbon clusters C-60 in external electrical field have been obtained. In this case three dimensional structure of the potential barrier at the fullerene surface was taken into account. It is shown that preexponential multiplier is steppe depending on the strength of external electrical field with exponent degree equal m+1, where m is magnetic quant number. In general case for weak external electrical fields it has been shown, that the main contribution to emission probability is made by states with m=0 and that is character for autoemission of negative ions. It is necessary to point out for comparison that preexponential multiplier for metal surfaces has square depends on external electrical field (Fauler-Nordheim formulae).

- K-VI/P19** **NANOFABRICATION OF CARBON BASED MASKS FOR SELECTIVE GROWTH ON SEMICONDUCTOR SURFACES**, A. Avramescu, A. Ueta, K. Uesugi and I. Suemune, Res. Inst. Elect. Sci, Hokkaido University, Sapporo 060, Japan
A new method to make masks for low temperature selective growth or selective etching on the semiconductor surfaces will be presented. Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) being used as main tools in this purpose open the possibility to readily combine the advantages of both of them and have the wide range access up to ~ 1 mm of the former and the high resolution up to ~ 1 nm of the latter. In the SEM, a very thin carbonaceous film was deposited on p-type GaAs or Si by local decomposition of the residual oil molecules during repeated scans of the electron-beam on the surface. Further the carbonaceous film was patterned using an AFM. Applying an electric bias between the AFM tip and the substrate does patterning the 2-3nm-thick carbon based thin film as the tip is moved at 1-2 $\mu\text{m/s}$. As a result the film is anodized on nanometer scale areas and could be easily removed by immersing in HCl.
Dependence of the linewidth, height of the anodized area and depth of the final patterns on the applied bias was investigated. A minimum linewidth of 22 nm was obtained. The patterned masks were successfully used for selective area growth of ZnS and ZnSe.
- K-VI/P20** **FIELD EMISSION FROM NANOCARBONS AND NANOCARBONS WITH CVD CARBON COATING**, A.N. Andronov, S.V. Robozov, State Technical University, 195251, St.Petersburg, Russia; S.K. Gordeev, Central Research Institute of Materials, 191014, St.Petersburg, Russia; A.I. Kosarev, A.I. Vinogradov, A.F.Ioffe Phys.-Technical Institute, 194021, St.Petersburg, Russia
Field emission was studied from wafers of different nanocarbons (NC) and nanocarbons with CVD carbon coatings (NC+C). NC studied have skeleton carbon structure involving graphite or diamond like clusters hydrogen soaked in some samples. These nanomaterials were fabricated by special chemical synthesis in solid state. Nanopore concentration was in the range of 30...50%. CVD coating was deposited by plasma enhanced CVD at frequency 58 MHz and substrate temperature $T_s = 220^\circ\text{C}$ from hexane-hydrogen mixture.
Scanning secondary electron emission (SEE) measurements were performed before and after field emission measurements. Integral current-voltage characteristics $I(V)$ were measured at 10^{-8} Torr pressure and cathode-anode distance of 45 micron. NC samples demonstrated emission threshold (10^{-9} A) at field $E_{th} = 2$ V/micron. Carbon coating resulted in decreasing emission threshold field and the best characteristics were observed in NC+C structure, sample NP-B, $E_{th} = 0.25$ V/micron. The emission can be described by F-N law in the range of field studied in NC samples and only in high field region in NC+C samples. $I(V)$ curve of NP-B sample revealed different low field and high field parts, that is an indication on possible change of emission mechanism.
- K-VI/P21** **THE STUDY OF CARBON NANOTUBE PHASE TRANSITIONS BY BALL MILLING PROCESSING**, Y.B.Li, B.Q. Wei, J. Liang, D.H. Wu, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China
Since carbon nanotube was discovered in 1991, lots of researchers on structure changes of multi-shell carbon nanostructures have been done under different treatment, such as electron bombardment, high-temperature treatment and laser irradiation. In this paper, the study on morphology changes of carbon nanotubes with mechanical impact acting as driving force were carried out. The pure carbon nanotube powders fabricated by catalytic pyrolysis method were milling for different time in a high-energy mill, and the samples were detected by HRTEM.
The results indicate that some carbon nanotubes are broken under the action of steel ball impact, and large quantities of carbon onions are formed. On the basis of observation of carbon nanotubes, the carbon onion formation mechanism that carbon onion is formed at the end of carbon nanotube is discussed.
Moreover, some crystals were obtained in the samples. The lattice distance and the SAED pattern of these crystals are in accord with that of diamond.
- K-VI/P22** **FABRICATION OF ALUMINIUM-CARBON NANOTUBE COMPOSITES AND THEIR ELECTRICAL PROPERTIES**, C.L. Xu, B.Q. Wei, R.Z. Ma, J. Liang, X.K. Ma, D.H. Wu, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China
In this paper aluminium-carbon nanotube composites were fabricated by the method of powder metallurgical and hot-pressing processes. The microstructure characteristics, distribution of carbon nanotubes in aluminium matrix were investigated. The electrical resistivities of the composites at room temperature and at low temperature were measured. The measurements show that there is no effect of carbon nanotubes on the electrical resistivity at room temperature. In low temperature region the following phenomenon were found: from room temperature to -80K the composites exhibit the typically metallic decrease of the electrical resistivity with the reduction of the temperature; at about 80K their resistivities are abruptly dropped more than 90%; at lower temperature the resistivity is no more fluctuated.
- K-VI/P23** **A PARAMETRIC STUDY OF THE OPTICAL PROPERTIES OF CN_x THIN FILMS DEPOSITED BY A RF PLASMA BEAM**, G. Dinescu, E. Aldea, B. Mitu, C. Tanase, National Institute for Laser, Plasma and Radiation Physics, Magurele MG-36, Bucharest, Romania; A. de Graaf, M.C.M. van de Sanden, Department of Applied Physics, Eindhoven University of Technology, The Netherlands
The carbon nitride thin films are of large interest as regarding their possible applications in hard coatings, optics and microelectronics. CN_x thin films have been deposited by using a capacitively coupled RF plasma beam generated in nitrogen with graphite electrodes in various experimental conditions: different percentages of N_2 in Ar, gas pressure in the range 0.1-1 torr, substrate temperature in the range $30-400^\circ\text{C}$ and supplementary DC bias in the range $-200\text{V} \div +200\text{V}$.
Previous studies by FTIR spectroscopy and XPS spectroscopy have proved the incorporation of nitrogen and the presence of different nitrogen to carbon bond types. The X-Ray Diffraction and Transmission Electron Microscopy studies have shown that the films are amorphous and grown in a columnar structure. In the present work results of optical measurements of the deposited films are reported. The films have been investigated by means of UV-VIS absorption spectroscopy and FTIR measurements in order to find the dependencies of optical bandgap, refractive index and extinction coefficient upon the deposition conditions.
- K-VI/P24** **WITHDRAWN**
- K-VI/P25** **OPTICAL STUDY OF BONDED AND NON-BONDED HYDROGEN IN DIAMOND-LIKE CARBON**, V.I. Ivanov-Omskii and S.G. Yastrebov, A.F. Ioffe Physical-Technical Inst, 194021 St.Petersburg, Russia
Properties of Diamond-Like Carbon (DLC), which makes it attractive for various applications originate from hydrogen bound to carbon skeleton. DLC films were deposited onto KBr and silicon substrates by DC magnetron sputtering of graphite in argon-hydrogen (4:1) plasma. The ellipsometrical measurements (6328 nm) together with IR spectroscopy (2-20 μm) were made. To proceed the dielectrical permittivity in IR range, ellipsometric data and IR absorption ones were taken into account in the course of *ab-initio* calculations. The concentration of bound hydrogen was determined by an analysis of imaginary part of the permittivity for the spectral range of $2900-3000\text{cm}^{-1}$, which corresponds to IR absorption bands attributed to C-H stretch modes. Concentration of bound hydrogen has trend to decrease after increase of annealing temperature and reached zero for 1h annealing at 450°C . This is in a good agreement with literature data. An estimation of activation energy of chemical reaction between bounded and quasi-free hydrogen was shown to be $(0.5 \pm 0.2)\text{eV}$. Quite unexpected the restoration of the dielectrical permittivity was observed after room-temperature treatment of the films with time constant of the order of 2-3 days. An estimation of returning rate of quasi-free hydrogen to its bonding sites is carried out. Two-well potential diagram for the reaction bonded - (quasi-free hydrogen) is suggested. This work was supported in part by RFBR grants N97-03-32273, Russian Program Physics of Solid State Nanostructures and "Fullerenes and Atomic Clusters"(N94007), the US Department of defense.

- K-VI/P26** PERCOLATION THROUGH COPPER-DOPED DIAMOND-LIKE CARBON, A.B. Lodygin, V.I. Ivanov-Omskii, V.I. Siklitsky, A.V. Tolmachev and S.G. Yastrebov, A.F. Ioffe Institute, 194021 St.Petersburg, Russia
A modification of Diamond-Like Carbon (DLC) properties by introduction of metal nanoclusters is of much interest by possible applications of the material to nano-electronics. The DLC films were grown by ion co-sputtering of graphite and copper targets in 80% Ar and 20% H₂ plasma. The copper concentration was varied within the range 0-24 at.%. We present the study of optical transmission spectra (0.6-5 eV), Transmission Electron Microscope (100 keV) images of copper-born clusters embedded into DLC matrix, DC room-temperature conductivity and X-ray (1.541Å) scattering of the samples. Fractal dimensions and sizes of scatterers (copper-based clusters) were plotted as functions of total copper concentration. It was possible to derive a fractal dimensionality of the elements of percolation network as well as. The results evidence the existence of percolation network with elements of fractal structure with parameters depending on the copper content. It was shown that at lower copper contents ($x < 14-16$ at.%) the flake-like copper-containing fragments exert primary influence on the material's properties. At higher copper concentrations the formation of three-dimensional elements becomes more favourable. Sizes and geometrical characteristics of the network elements obtained with the above methods are discussed in the frame of fluctuation theory of clusters nucleation and kinetic theory of their growth. This work was supported in part by "Fullerenes and Atomic Clusters" grant 94007, RFBR grants N 97-03-32273-a, N 97-02-18110-a, State Russian Program "Physics of Solid State Nanostructures" and the US Department of defense.
- K-VI/P27** AN INVESTIGATION OF THE THERMAL PROFILES INDUCED BY ENERGETIC CARBON MOLECULES ON A GRAPHITE SURFACE, M. Kerford and R.P. Webb, S.C.R.I.B.A., School of Electronic Engineering, Information Technology and Mathematics, University of Surrey, Guildford, Surrey, GU2 5XH, UK
Molecular Dynamics simulations are used to investigate the velocity distributions of a graphite lattice after being struck by carbon molecules. A temperature profile can be inferred from this velocity distribution and the 'cooling' down time of the ensuing thermal spike has been investigated. A range of molecule shapes and sizes for different energies is investigated and the applicability of traditional models of spike quenching. The kinetic energy from the impacts are seen to spread across the surface much faster than into the material in line with the properties of the thermal diffusivity. A rapid phonon transport mechanism is seen to propagate out from the impact site. The velocity of the wave is independent of the molecule size, shape and energy but the amplitude and start time is dependant upon all of these parameters.
- K-VI/P28** FUNCTIONAL MATERIALS: FILM/BULK COMPOSITES SELF-ORGANIZING FROM CARBON MOLECULES/CLUSTERS AND MICRO/NANOCRYSTALLINE OXIDE METAL WITH NEW ELECTRONICS, OPTOELECTRONICS, MAGNETO-OPTICS PROPERTIES, E. Buzaneva, A.D. Garchinsky, Y.I. Prilutsky, V.F. Kovalenko, National T. Shevchenko University, Vladimirska St. 60, 252033 Kiev, Ukraine; B.D. Shanina, A.A. Konchits, Institute of Semiconductor Physics, Science Pr. 45, 252130 Kiev, Ukraine; M.Y. Katsai, M.A. Voronkin, Institute of Superhard Materials, Stankozavodskaya 43, 252046 Kiev, Ukraine; G.G. Andrievsky, Institute for Therapy of the Academy of Medical Sciences of Ukraine, Postysheva St. 2a, 310116 Kharkov, Ukraine
Using the experimental results and theoretical prediction of possible ways of film/bulk composites self-organization from carbon molecules/clusters and micro/nanocrystalline oxide metal three self-organization aspects are developed: C₆₀ molecules/clusters assembly from dimers, trimers or long chains occurring in solid composite films with metal and oxide metal (Er, Fe) under influence of light on solutions; Bulk 3D-polimerized microcrystalline C₆₀±X solid under high pressure and low temperature heating; C₆₀±X-fullerene, nanotubes, nanographite, nanodiamond and doping elements organized in various layered combinations under high pressure and heating. Theoretical are predicted and confirmed experimentally particularly new electronics, optoelectronics, magneto-optics properties of new composites.
The semiconductor photoconductivity and visible photoluminescence of the thin films from C₆₀±X with sp¹ CH, sp³ CH₂/CH₃ and sp³ C-C groups and nanocrystalline Fe were observed.
The composites from microcrystalline C₆₀±X with/without metal oxide, self-organized under the pressure P=8 GPa at T= 1720 K present a new structural phase of nano-molecular carbon, which has simultaneously metal conductivity and semiconductor photosensitivity. The change of the exposure duration of composite under pressure increases conductivity and decreases photosensitivity when the time duration grows. The composites which was exposed minimal time demonstrate very strong anisotropy of this effect: it is observed only by the orientation of the composite sample with the direction of uniaxial compression parallel to the vector of magnetic component of microwave field in the cavity. The deviation of this orientation only by one degree leads to disappearance of the optical amplification of the EPR signal for conduction electrons. In fact, the composite sample acts like linear wave-guide in the cavity and was the optical switch of the microwave absorption.
- K-VI/P29** POLYCRYSTALLINE DIAMOND FORMATION BY POSTGROWTH ION BOMBARDMENT OF SPUTTER-DEPOSITED AMORPHOUS CARBON FILMS, P. Patsalas, S. Logothetidis, P. Douka, M. Gioti, G. Stergioudis, Ph. Komninou and Th. Karakostas, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
Postgrowth Ar⁺ ion beam bombardment (IBB) of amorphous carbon films, deposited by rf magnetron sputtering on c-Si(100), with energies above 1 keV, induces several structural modifications in the films, including the formation of diamond grains as well as other carbon and hexagonal SiC phases. Detailed X-ray diffraction (XRD) measurements in both conventional (Bragg-Brentano) and grazing incidence geometry and high resolution transmission electron microscopy (HRTEM) were used to study the phases that resulted by IBB and to understand the possible mechanism that transforms the amorphous carbon phases to crystalline diamond. The ratio of diamond to graphite XRD lines intensity in IBB films was found to be larger when the as-grown films were rich in sp² sites suggesting that "disordered" graphite-like phases favored more the formation of diamond grains than tetrahedrally bonded or other carbon phases did. These results are also supported by HRTEM and X-ray reflectivity studies. The latter shows the increase in film density upon IBB. The effect of IBB parameters, such as ion flux and energy, on the crystalline diamond nucleation and grain size were studied and discussed in relation with the carbon phases and structures observed in the as grown films.
- K-VI/P30** ELECTRICAL BEHAVIOUR OF METAL/a-C/Si AND METAL/CN/Si DEVICES, E. Evangelou, N. Konofaos, S. Logothetidis* and M. Gioti, * Applied Physics Laboratory, Physics Department, University of Ioannina, 45110 Ioannina, Greece; *Physics Department, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
Electrical characterisation for devices having the Metal/Carbon/Si structure took place. Amorphous carbon films rich in sp³ bonds were grown onto n-type Si substrates by RF magnetron sputtering at room temperature. A variety of films were grown under different deposition conditions to create different sp³ and sp² configurations in order to examine their contribution to the performance of electronic devices. Suitable metalisation was used to fabricate devices which were then characterised electrically. Electrical characterisation with I-V, C-G-V and G-w techniques showed temperature dependent currents through the devices which increase rapidly when forward bias is applied. This behaviour was dependent on the sp³-sp² contents of the films. The devices were Metal-Insulator-Semiconductor diodes with a defect insulator resulting in creating thermally stimulated currents through the devices. The effect of nitrogen introduced in the growth process to produce carbon nitride films was also examined. Different amounts of nitrogen were used and the same characterisation process for a variety of samples took place. The films were nearly perfect insulators and the corresponding devices showed a clear MIS behaviour. Thus, the room temperature deposition technique produced films which can be used in devices, their electronic characteristics being dependent on the C-C bonding configuration. Moreover it is shown that the nitrogenated films made under certain conditions act as insulating parts of the devices.

- K-VI/P31** SYNTHESIS OF THE DIAMOND CRYSTALS FROM OXYGEN-ACETYLENE FLAME ON THE Si AND Mo SUBSTRATES AT LOW TEMPERATURE, V. A. Cherepanov, E.V. Grigoryev, V. N. Savenko, D. V. Sheglov, A. V. Matveev, A. S. Zolkin, Novosibirsk State University, 630090 Novosibirsk, Russia
Diamond polycrystal films and particles were synthesized by deposition from oxyacetylene flame on the monocrystal silicon and molybdenum substrates under atmospheric conditions. The best results: a polycrystalline diamond film and perfect octahedral crystals, were obtained at $R(O_2/C_2H_2) = 1.0$, gas flow rate $F = 2.2$ l/min, distance between flame-corn and the surface of the substrate $d = 2$ mm on Mo - substrates. Raman shift: 1331 cm^{-1} , the crystal growth rate: $50\text{ Å}^0/\text{c}$. The thermal flow to the surface of the substrate during the process of growth of crystals was measured. It has been stated that diamond particles on molybdenum and silicon surfaces can be grown at the surfaces' temperature: $T = 873 - 1123\text{ K}$ which is lower by about $100 - 150\text{ K}$ than the temperature reported in the known studies of the flame method. Studies of fine diamonds particles on the silicon substrates have been carried out of the luminescence under the action of electrons with the energy of 20 keV .
- K-VI/P32** ULTRAFAST RELAXATION PROCESSES IN CARBON-BASED MATERIALS, Y.M. Farztdinov, Yu.E. Lozovik, Yu.A. Matveets, A.L. Dobryakov, D.V. Lisin, Institute of Spectroscopy, RAS, Troitsk, Moscow Region, 142092, Russia; S.A. Kovalenko, N.P. Ernsting, Humboldt-Universität zu Berlin, Germany, and G. Marowsky, Laser Laboratorium Göttingen, Germany
The ultrafast relaxation processes in a number of carbon based materials: solid C_{60} ; new hard carbon phase, obtained after heat treatment of C_{60} to 1550 K at 13 GPa nonhydrostatic pressure; and amorphous carbon films, obtained under the treatment by powerful IR-pulses of polyacrylonitrile films, were studied in the energy range $1.6 - 3.4\text{ eV}$ by pump-supercontinuum probe technique with 40 fs time resolution. To find out the similarity and distinction of carbon based materials in their structural, electronic, and nonlinear properties we investigated the dependence of relaxation rate on probing wavelength and pumping pulse intensity. The samples were excited by optical pulses with duration of 50 fs and with energy of $\hbar\omega_{\text{pump}} = 2.34\text{ eV}$. The pump pulse energy density was varied in the region of $4-20\text{ mJ/cm}^2$.
- K-VI/P33** PHASE TRANSITION AND SELF-ASSEMBLING PROCESSES IN CLUSTERS OF ULTRADISPERSE DIAMOND, A.E. Aleksenskii, M.V. Baidakova, V.I. Siklitsky, A.Ya. Vul', Ioffe Physico-Technical Institute, 194021 St.Petersburg, Russia
Comprehensive study of diamond-graphite the phase transition (PT) in clusters of ultradisperse diamond (UDD) produced by detonation synthesis has been developed. The main point of attention is the PT on samples differing in the kinetics of cooling of detonation product. The PT was carried out at heating in inert atmosphere and in hydrogen at temperatures $720\text{ K} - 1400\text{ K}$. For characterization of UDD Raman scattering (RS), X-ray experiments (XR) were used. RS and XR results allowed us to conclude that UDD is cluster with the crystal structure of diamond, and typical size of one is about 40 Å independently from of the kinetics of cooling. It was determined, that contained in UDD small amount amorphous diamond and graphite are situated on the surface of diamond core. The new model in which an UDD cluster is a diamond core (with sp^3 bonds) and shell (with sp^2 bonds mainly) has been considered. It is supposed that the difference in the shell structure of UDD cluster is the consequence of the reverse transition diamond-graphite at cooling of detonation product. It is confirmed that UDD clusters are fractal objects, and we have found that not only the type but also the fractal dimension depends on the rate of cooling of detonation product. It is suggested that the first stage of the PT depends on the structure of shell, and the onion-like carbon and graphite network formation during the diamond annealing is a self-assembling process. The great influence of oxidation method of detonation product on cluster structures (the thickness of cluster shell and sp^2/sp^3 ratio) has discovered.
- K-VI/P34** MOLECULAR MODELING OF FULLERENES AND IRON COMPOUNDS COMPLEXES AIMED TO SELECT PROPER REAGENTS AND REACTION CONDITIONS, P. Byszewski*, E. Kowalska, Institute of Vacuum Technology, ul. Douga 44/50, 00-241 Warsaw, Poland (* also at Institute of Physics PAS, al.Lotnikow 32/46, 02-668 Warsaw, Poland) Z. Kucharski, Institute of Atomic Energy, 05-400 Swierk, Poland
We applied the semiempirical quantum chemistry ZINDO method in order to evaluate binding energy of fullerenes with several ferrocene derivatives that might be formed in ferrocene solution in toluene or benzene. It was found that polymerization of cyclopentadiens with solvent molecules might lead to freeing of iron ions which in turn might be captured by fullerenes if they are present in the solution. We have optimized possible fullerene-Fe complexes of various structures and spin states and calculated their energy. Information on the bonding energy helps us to estimate thermal treatment conditions necessary to purify the samples of the oligomers formed during the reaction of cycloadducts to fullerenes. The calculations will be compared with the experiment results.
- K-VI/P35** ^{161}Dy MÖSSBAUER STUDY OF $\text{Dy}@C_{82}$, Yu.S. Grushko, E.G. Alekseev, V.S. Kozlov, L.I. Molkanov, St. Petersburg Nuclear Physics Institute, Gatchina 188350, Russia and H. Giefers, M. Strecker, G. Wortmann, Universität-GH Paderborn, Fachbereich Physik, 33095 Paderborn, Germany
The off-center in-cage location of lanthanide atoms (Ln) in endohedral metallofullerenes is of actual interest with respect to open questions about Ln-fullerene charge transfer, temperature dependence of the magnetic- dipole and electric-quadrupole moments of Ln ions with unfilled 4f-shell and the supposed rich dynamic behavior of these systems[1]. We report on the first observation of resonant absorption of 26 keV gamma rays in $^{161}\text{Dy}@C_{82}$. The unusually low recoil-free absorption probability, which hampered recent trials to observe Mössbauer effect in endohedral metallofullerenes with ^{153}Eu (103 keV) [2] and with ^{155}Gd (86 keV) [3], is discussed in connection with structural and dynamic characteristics of $\text{Ln}@C_{82}$ derived from EXAFS studies [3-5]. The observed hyperfine interaction will be discussed with respect to above mentioned questions.
[1] W. Andreoni et al., in: Fullerenes and Fullerene Nanostructures (World Scientific, Singapore 1996), p.205. [2] Yu.S. Grushko et al., Mol. Mat., 1996, 7, pp. 115-118. [3] H. Giefers et al., these abstracts. [4] M. Nomura, et al., Physica B 208&209 (1995) 539. [5] C.-H. Park et al., Chem.Phys.Lett. 213, (1993) 196.- Work is supported by Russian State Program „Fullerenes and Atomic Clusters” and the DFG (Wo-209/10).

E-MRS'98 SPRING MEETING



SYMPOSIUM L

Nitrides and Related Wide Band Gap Materials

Symposium Organizers

- | | |
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| J.-Y. DUBOZ | Central Research Lab., Thomson-CSF, Orsay, France |
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SYMPOSIUM L

Tuesday June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I - Optical Properties

Chairperson: J.Y. Duboz, Thomson CSF, Orsay, France

- L-I.1** 9:00-9:30 - Invited - **LUMINESCENCE IN III-NITRIDES**, **B. Monemar**, Dept of Physics and Measurement Technology, Linköping University, 58183 Linköping, Sweden
In this talk we present an overview of some issues related to radiative recombination processes in III-nitrides. Intrinsic excitonic recombination is important for GaN as well as for quantum structures based on AlGaIn/GaN and GaN/InGaIn, in particular the dynamics of these excitonic processes will be discussed, in relation to the disorder present in the structures. Quantum wells as well as heterojunctions will be discussed. Defect related radiative recombination processes are generally the key to the identification of the corresponding defects. Here photoluminescence data are very important in correlating dopants and their binding energies with the corresponding optical signatures. A critical evaluation of the present understanding of these optical spectra will be given for donors as well as acceptors in GaN. The importance of deep level defects and complexes will also be discussed.
- L-I.2** 9:30-9:50 **TEMPERATURE DEPENDENCE OF OPTICAL CONSTANTS IN GaN AND GaInN**, **U. Tisch**, J. Salzman, E. Finkman, G. Bahir, TECHNION, Haifa 32000, Israel; A. Aber, S. Denbaars, L. Coldren, University of California, Santa Barbara, CA 93106, USA, and W. Van der Stricht, University of Gent, St. Pietersnieuwstraat 41, 9000 Gent, Belgium
GaN-based lasers operate at active layer temperatures substantially higher than room temperature. Knowledge of the optical constants of the heterostructure constituents is needed in order to optimize the waveguide design. In this work, spectroscopic ellipsometry and spectrophotometric measurements were performed on GaN and GaInN in the temperature range of 77⁰K-550⁰K with the purpose of studying the material dispersion at temperatures relevant to laser operation. The layers were grown on (0001) sapphire substrates by Organometallic Vapor Phase Epitaxy. A three or four layer model makes possible to describe in a unified way the optical constants of GaN or GaInN grown at different laboratories. We thus obtain reliable values of complex refractive index spectra (n and k) in the energy range of 0.9-4.5 eV, and their temperature dependence. Excitonic features persist at temperatures above room temperature in bulk GaN. Bandgap and linewidth dependence on temperature are extracted.
- L-I.3** 9:50-10:10 **OPTICAL PROPERTIES OF HEXAGONAL GaN, AlN AND Al_xGa_{1-x}N FILMS IN THE SPECTRAL RANGE 3-20eV**, **T. Wethkamp**, K. Wilmers, M. Cardona, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany; and N. Esser, C. Cobet, W. Richter, Institut für Festkörperphysik, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany, and O. Ambacher, Walter-Schottky-Institut, TU München, Am Coulombwall, 85748 Garching, Germany
A variety of GaN, AlN and Al_xGa_{1-x}N films grown on c-Al₂O₃ by MBE and MOCVD has been investigated by spectroscopic ellipsometry in the vacuum-ultraviolet spectral range using synchrotron radiation from the Berlin electron storage ring BESSY. Measurements were taken at room temperature and low temperatures down to 100K in the spectral range 3-20eV. Surface morphology and crystalline quality strongly affect the absolute values of the measured effective dielectric function <ε>. However, energy positions of features in <ε> remain the same. By comparison to band structure calculations these can be assigned to interband transitions at distinct points of the Brillouin zone. The dependence of these critical points on temperature and composition x for Al_xGa_{1-x}N are determined. For AlN features are observed near the band gap similar to known features in reflectance spectra of GaN which are attributed to the strain dependent A, B, C valence band splittings.

10:10-10:30

BREAK

SESSION II - Exciton Physics

Chairperson: B. Gil, GES, Université de Montpellier, France

- L-II.1** 10:30-11:00 - Invited - **ULTRAFAST PHYSICS IN NITRIDES**, M.R. Hofmann, R. Zimmermann, A. Euteneuer, and **W.W. Rühle**, Fachbereich Physik und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität, 35032 Marburg, Germany
The potential of ultrafast, nonlinear and linear spectroscopy for the investigation of exciton resonances in GaN is demonstrated.
Four-wave-mixing is shown to be a very powerful tool to accurately determine the energies of the intrinsic exciton resonances, the biexcitonic binding-energy, and the splitting of A- and B-excitons. Exciton - exciton and exciton - acoustic phonon scattering-rates were determined [1,2] and will be compared with results of other groups. [3,4] The particularities of GaN with respect to other compound semiconductors will be discussed in detail.
In addition, exciton relaxation is studied by means of time-resolved photoluminescence measurements.
[1] R. Zimmermann et al., MRS Internet J. Nitride Res. 2, 24 (1997) and Proc. of the E-MRS 1997 Spring Meeting
[2] R. Zimmermann et al., Phys.Rev. **B56**, R12722 (1997)
[3] A.J. Fischer et al., Phys.Rev. **B56**, 1077 (1997)
[4] S. Pau et al., Phys.Rev. **B56**, R12718 (1997)

L-II.2 11:00-11:20

INTENSITY AND WAVELENGTH DEPENDENCE OF χ^3 CLOSE TO THE EXCITONIC RESONANCES OF GaN, H. Haag, P. Gilliot and B. Hönerlage, Groupe d'Optique Nonlinéaire et d'Optoélectronique, I.P.C.M.S., UMR 380046 CNRS-ULP-ECPM, 23 Rue du Loess, B.P. 20CR, 67037 Strasbourg Cedex, France; O. Briot and R.L. Aulombard, Groupe d'Etude des Semiconducteurs, URA 357 CNRS-Université de Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

We perform degenerate four-wave mixing measurements in a two beam configuration at 2K on a 0.2 μ m thick GaN sample, grown by MOCVD on a sapphire substrate. A nanosecond excimer laser pumps a spectrally narrow dye laser, tuneable near the excitonic resonances. We study the intensity variation of the diffracted beams as a function of the photon energy and intensity of the exciting beams. Results show the contributions of the A- and B- excitons to the χ^3 value. In addition, a saturation occurs which depends on the wavelength of the exciting photons. Finally, we excite our sample with a third beam at 308 nm and study the influence of the carrier populations on the χ^3 value.

L-II.3 11:20-11:40

STUDY OF HEXAGONAL GaN BY FEMTOSECOND-EXCITATION CORRELATION MEASUREMENT AND DEGENERATE FOUR-WAVE-MIXING, S. Pau, J. Kuhl, F. Scholz*, C. Haerle*, M.A. Khan** and C.J. Sun**, Max-Planck-Institut, Heisenbergstrasse 1, 70569 Stuttgart, Germany; *Universität Stuttgart, 4. Physikalisches Institut, Kristalllabor, 70550 Stuttgart, Germany; **APA Optics Inc., 2950 N. E. 84th Lane, Blaine, Minnesota 55449, USA

We report here low temperature spectral and temporal study of carriers and excitons dynamics of GaN by femtosecond excitation correlation (FEC) measurement and degenerate four-wave-mixing (DFWM). FEC spectroscopy is a powerful technique to study incoherent emission dynamics with temporal resolution limited only by the excitation pulse width and DFWM is a complementary technique which allows accurate determination of the exciton dephasing time, i.e. the coherent properties of the material transitions. In the FEC experiment, the two cross polarized excitation beams (pulse width of 150fs), chopped at two different frequencies, are set to be 20 meV (A exciton binding energy) above the A exciton energy to generate cold e-h pairs at the band-edge, and the spectrally resolved PL at the A and DX exciton energies are detected by lock-in technique at the sum frequency as a function of time delay, τ , between the two pulses. The PL and FEC spectra show evidences of nonlinear effects which we attribute to impurity saturation and bimolecular recombination processes. A quantitative theoretical analysis of the decay curves using a rate equation model will be presented and explains much of the FEC results. We also perform DFWM on GaN as a function of energy, excitation density and temperature. By measuring the scattering efficiency of both the 3rd and 5th order diffracted beams, we estimate the value of the effective nonlinear susceptibilities at the A exciton energy at 10 K to be $|\chi_{eff}^{(3)}| = 2 \times 10^{-11}$ esu and $|\chi_{eff}^{(5)}| = 0.5 \times 10^{-17}$ esu.

L-II.4 11:40-12:00

EXCITON RECOMBINATION IN GaN AND CAPTURE IN InGaN QUANTUM WELLS IN THE PRESENCE OF AN ELECTRIC FIELD OR UNDER INTENSE PHOTOEXCITATION, F. Binet, J.Y. Duboz, N. Laurent, C. Grattepain, Laboratoire Central de Recherches, Thomson-CSF, 91404 Orsay, France; F. Scholz, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

The progress in the field of electrical and optoelectronic devices based on GaN and related alloys have been spectacular. The performance of LEDs and LASERS is remarkable with regard to the crystallographic quality of the material. This may be attributed to the strength of excitonic effects in GaN based materials and we thus focus our attention on basic aspects of exciton recombination in GaN.

Photoluminescence studies have been performed in GaN bulk layers and InGaN/GaN quantum well structures grown by MOCVD on sapphire substrates. In a bulk GaN sample with two electrical contacts, we follow the evolution of the bound exciton, free exciton and Donor-Acceptor lines as a function of temperature and electric field. We will show the effect of the field on the localization and on the ionization of excitons. The interplay between field effects and thermal excitation will be presented. Under intense optical excitation by a pulsed quadrupled YAG laser at low temperature, we observe the ionization of excitons and we can determine the Mott transition. The peak position red shifts in agreement with the theoretical band gap renormalization. On the low energy side of the GaN luminescence line, new features are apparent. Their origin will be discussed in relation with phonons and high carrier density effects. In InGaN/GaN quantum well structures, we study the transfer of carriers between the photopumped GaN barrier and the InGaN well. Using a structure with two InGaN quantum wells with different compositions, we were able to measure the capture probability of excitons in the wells.

L-II.5 12:00-12:20

TIME-RESOLVED SPECTROSCOPY OF NITRIDE SEMICONDUCTORS, M. Pophristic, F.H. Long, Department of Chemistry, Rutgers University, Piscataway NJ 08854-8087, C.A. Tran, R.F. Karlicek Jr., Z.C. Feng, I. Ferguson, EMCORE Corporation, Somerset NJ 08873, USA

We have used picosecond time-resolved emission and femtosecond transient absorption to investigate films and MQWs of InGa_xN at room temperature. The film was 300 Å thick and both the film and the MQWs contained In_{0.22}Ga_{0.78}N with x=22%. In both the MQWs and the film the emission lifetime increased with laser fluence. This effect is attributed to the saturation of recombination centers at high laser powers. Lifetimes longer than one nanosecond were observed in the MQWs at room temperature, with the highest laser powers. In both the films and MQWs the emission lifetime became much shorter at shorter emission wavelengths. The dramatic change in the observed emission lifetime with wavelength is attributed to an increase in the density of states at higher energies and a subsequent increase in the decay rate. We will also present time-resolved measurements of yellow emission from 6H- and 4H-SiC at room temperature.

12:20-14:00

LUNCH

Tuesday June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-Midi

SESSION III - Growth: MOCVD and HVPE**Chairperson:** T. Honda, Kohgakuin University, Tokyo, Japan

- L-III.1** 14:00-14:30 - Invited - **CURRENT STATUS OF GaN PRODUCTION MOVPE REACTORS**, M. Deschler, D. Schmitz, M. Heuken, **H. Juergensen**, AIXTRON AG, Kackertstr. 15-17, 52072 Aachen, Germany
Red, green, blue and white light emitting diodes are currently entering the commercial market for applications in light systems. Blue lasers will open new possibilities for DVD systems. All these devices can be realized by GaN based heterostructures grown by MOVPE. Large scale multiwafer MOVPE reactors were used to grow these layer structures on an industrial scale. Recent progress and future trends will be discussed on the basis of physical process models which are compared to experimental results. High precursor yield, extreme uniformity and the resulting minimized cost of ownership were demonstrated by discussing typical LED structures consisting of GaN:Mg, AlGaIn and InGaIn. The material quality touches the currently known physical limits in terms of purity, optical and electrical properties.
- L-III.2** 14:30-15:00 - Invited - **GROWTH OF HIGH-EFFICIENCY InGaIn MQW BLUE LEDs USING LARGE-SCALE PRODUCTION MOCVD REACTOR AND THEIR CHARACTERIZATION**, **C.A. Tran**, R.F. Karlicek, Jr., R. Stall, M. Schurman, I. Ferguson, A. Onsiniski and J. Rajer, Emcore Corp, 394 Elizabeth Avenue, Somerset NJ 08873, USA
In this work we report the epitaxial growth of blue LEDs with wavelengths longer than 450 nm in a large scale production MOCVD reactor. The growth of candela-class blue LEDs is carried out in a large-scale production MOCVD reactor equipped with *in-situ* reflectance spectroscopy. The reactor is capable of yielding of 6 x 2" wafers for each run. Properties of n-type, p-type GaN, AlGaIn as well as the phase separation of indium in InGaIn MQW will be described and discussed. High electron carrier mobility (650 cm²/vs @ 300K) in undoped GaN, high hole concentration (1e18 cm⁻³) in p-GaN and photoluminescence emission longer than 520 nm in InGaIn/ GaN MQW were achieved. The LEDs have active layer composed of a stack of InGaIn/GaN wells clad by AlGaIn on p-contact side. The forward voltage is as low as 3V and the brightness at 20 mA is better than one candela for the blue LEDs (460nm). The impact of this work is that high brightness Blue and Green LEDs based on InGaIn/GaN material can be produced at high volume in a multi-wafer production MOCVD reactor.
- L-III.3** 15:00-15:20 **CONTROL OF THE NUCLEATION OF MOVPE GaN ON SAPPHERE USING A SiN COATING OF THE NITRIDATED SURFACE**, **P. Vennéguès**, B. Beaumont, S. Haffouz, H. Lahreche, P. De Mierry, and P. Gibart, Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique, Rue Bernard Gregory, Sophia Antipolis, 06560 Valbonne, France
The first stages of the growth of highly mismatched heteroepitaxial systems, as GaN on sapphire, mainly proceeds by the nucleation of 3D nuclei. The resulting structural threading defects are introduced to accommodate the misorientations between the nuclei. Using a SiN coating of the nitridated sapphire surface which modify the surface energy, it is possible to control the sizes and densities of nuclei and, therefore, to reduce the density of structural defects. We have studied, using Transmission Electron microscopy, the microstructure of both atmospheric and low pressure Metalorganic Vapor Phase Epitaxy GaN films on (0001) sapphire at different stages of the growth. After the nitridation of the sapphire surface at high temperature ($\approx 1000^\circ\text{C}$) which results in the formation of a thin AlN film, a flat continuous nucleation layer is deposited at low temperature (500-600°C). During the temperature rise up to the growth temperature ($\approx 1000^\circ\text{C}$), we observe the formation of islands with a characteristic truncated pyramidal shape. The subsequent growth is mainly lateral, leading to a smoothing of the surface after a thickness of about 500 nm. For an optimised SiN deposition time (30"), the resulting defect density is decreased down to the 10⁸cm⁻² range.
- L-III.4** 15:20-15:40 **GROWTH of GaN SINGLE CRYSTAL SUBSTRATES**, **O. Kryliouk**, M. Reed, T. Dann, T. Anderson, Chemical Engineering Dept., Univ. of Florida, Gainesville FL 32611, USA and B. Chai, Crystal Photonics, Inc., Orlando FL 32817, USA
We report on the successful growth of large area bulk GaN single crystals using the rapid growth rates obtainable with hydride vapor phase epitaxy (HVPE). Seed crystals were grown by MOCVD on (001) LiGaO₂ substrates, and HVPE deposition was conducted in the temperature range 850 to 950 °C and at atmospheric pressure with a growth rate 50 to 70 µm/hr. The key to obtaining high quality MOCVD GaN on LiGaO₂ is the initial surface nitridation step. It is believed that a surface reaction product is formed during nitridation that promotes recrystallization of the underlying LiGaO₂ and shows a lattice parameter very close to that of GaN. Furthermore, this reaction product serves as an efficient barrier for Li transport into the GaN. The surface of the MOCVD grown GaN was atomically flat (surface roughness $R_a=0.036$ nm) and the bulk microstructure was excellent as judged by TEM and HRXRD analysis. We developed methods of separating HVPE GaN from underlying LiGaO₂ substrate, leaving large area free-standing wafers of GaN. LRXRD spectra revealed the GaN (0002) and (0004) diffraction peaks. Growth studies and film characterization results of thick GaN films are presented. The surface morphology was determined by AFM, the structural quality was analyzed by TEM and XRD, while the composition was investigated by AES, SNMS, SIMS and ESCA.

SYMPOSIUM L

L-III.5 15:40-16:00

SPECTROSCOPY AND MICROSCOPY OF LOCALISED AND DELOCALISED EXCITONS IN InGaN-BASED LIGHT EMITTING DIODES AND EPILAYERS, K.P. O'Donnell, R.W. Martin, University of Strathclyde, Scotland; S.C. Bayliss and I. Fletcher, De Montfort University, England and W. Van der Stricht, P. Demeester, I. Moerman, University of Gent, Belgium

A comparison of the electroluminescence (EL) spectra and photocurrent (PC) spectra of commercial Nichia "chip-type" diodes was undertaken in order to clarify the energy relationship between localised and delocalised states. In addition the microscopy of diodes and epilayers was studied using comparative scanning electron microscopy (SEM), cathodoluminescence (CL) and energy dispersive X-ray (EDX) imaging.

A clear signature for the existence of localised states in inhomogeneously broadened optical spectra is the presence of a so-called "Stokes' shift" between absorption and emission peaks. This quantity requires careful definition when we compare EL (emission) and PC (equivalent to absorption) spectra of InGaN diodes. There is clear evidence for such a shift in our results. Contrary to some previous work, however, we find the shift to be insensitive to the mean In content in the active region of the devices.

An explanation of the optical results is found in a detailed picture of the microscopic nature of the InGaN alloy obtained using electron microscopy. Regions of relatively high In content are found within the matrix, on a size scale much larger than that of a quantum dot. For the first time, a coherent view of processes for light emission in semiconductor alloys emerges.

16:00-16:30

BREAK

SESSION IV - InGaN QW

Chairperson: Ch. G. Van der Walle, Xerox Parc, Palo Alto, USA

L-IV.1 16:30-17:00 - Invited -

OPTICAL PROPERTIES OF InGaN QUANTUM WELLS, S. Chichibu*, D. Cohen, M. Mack, A. Abare, P. Kozodoy, M. Minsky, S. Fleisher, S. Keller, J. Speck, J. Bowers, U. Mishra, L. Coldren, S. DenBaars, University of California, Santa Barbara, CA 93106, USA; K. Wada, NTT System Electronics Labs., Atsugi 243-0198, Japan; T. Deguchi, T. Sota, Waseda University, Shinjuku, Tokyo 169-8555, Japan; and S. Nakamura, Nichia Chemical Industries Ltd., Anan, Tokushima 774-8601, Japan; *also, Science University of Tokyo, Noda, Chiba 278-8510, Japan

Emission mechanisms of InGaN QWs grown on sapphire substrates were investigated. They showed various degree of potential inhomogeneity, which produced localized energy states. Both the Stokes-like shift (orders of hundred meV) and the decay time (orders of ns) changed remarkably around nominal InN molar fraction 0.2, which changes to nearly 0.08-0.1 for the strained InGaN. The spontaneous emission from the QWs was assigned as being due to the recombination of excitons localized at the potential minima, whose lateral size varied from less than 60 nm to 300 nm. Blueshift of the emission peak by increase of excitation level was explained to originate from combined effects of band-filling and carrier screening of the quantum confined Stark effect induced by the piezoelectric field. The lasing mechanisms of the cw InGaN MQW LDs having small potential fluctuation was described by the EHP picture while the inhomogeneous MQW LDs were considered to lase by EHP in segmented QWs or Q-disks. It is desirable to use entire QWs with small potential inhomogeneity as gain media for higher performance LD operation.

L-IV.2 17:00-17:30 - Invited -

THEORETICAL OPTICAL GAIN IN InGaN QUANTUM WELLS, T. Uenoyama and M. Suzuki, Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., 3-4 Hikaridai, Seika-cho Sourakugun, Kyoto 619-02, Japan

We review the optical gain of GaN/InGaN quantum well structures within a single particle picture and show the problem such that the large density of states for the conduction and valence bands due to the strong electronegativity and the weak spin-orbit coupling of the N atom caused the high threshold carrier density. Then, we evaluate the optical gain of GaN/InGaN quantum wells using a many-body approach to include the screening effect, band-gap renormalization, Coulomb enhancement and so on. Especially, the Coulomb interaction is a very important factor for wide-gap semiconductors, and the many-body approach makes it clear how the exciton, which is the electron-hole bound state, is related to the optical gain. In the two-band model where only the conduction and valence bands are adopted, the excitonic absorption peak is gone when the optical gain appears by increasing the carrier density. So, we can understand that the electron-hole bound state, so-called exciton, cannot produce the optical gain. Then, we will discuss how the optical gain is affected by the localized states in the band gap. This situation corresponds to the case where InGaN well layers have the localized states by the alloy-fluctuations of the In content and in experiments, it was recently found that this localized states played important role in the spontaneous emission.

L-IV.3 17:30-17:50

CARRIER CONFINEMENT IN GaInN/AlGaIn/GaN QUANTUM WELLS WITH ASYMMETRIC BARRIERS: DIRECTION OF THE PIEZOELECTRIC FIELD, Jin Seo Im, H. Kollmer, J. Off, F. Scholz, and A. Hangleiter, 4. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

Recently, there have been lively discussions about piezoelectric fields in wurtzite GaN-based quantum wells. We have demonstrated a dramatic reduction of the oscillator strength due to piezoelectric fields in GaN/AlGaIn and InGaIn/GaN quantum wells. In order to study this effect in detail we have now introduced additional AlGaIn barriers in GaInN/GaN quantum well structures. The carrier confinement in such structures depends crucially on the direction of the piezoelectric field with respect to the AlGaIn barriers. Our study using time-resolved photoluminescence spectroscopy reveals a different temporal and temperature behaviour as well as different energetic positions of the emission peaks depending on where the AlGaIn barrier is placed. In particular, the oscillator strength becomes much larger if an AlGaIn barrier is grown on top of the GaInN well. These experimental results can be consistently explained by the asymmetry induced through the piezoelectric field and allow us to determine the sign and magnitude of the field.

SYMPOSIUM L

POSTER SESSION I

Chairpersons: **B.K. Meyer**, University of Giessen, Germany and
M. Kamp, University of Ulm, Germany

18:00-20:00

See programme of this poster session p. L-21 to L-26.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-Midi

SESSION V - Growth: MBE

Chairperson: G. Feuillet, CEA-Grenoble, France

- L-V.1** 14:00-14:30 - Invited - **MOLECULAR BEAM EPITAXY GROWTH OF NITRIDE MATERIALS, N. Grandjean** and J. Massies, Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique, Rue Bernard Gregory, Sophia Antipolis, 06560 Valbonne, France
- III-V nitride layers are grown on c-plane sapphire substrates by molecular beam epitaxy (MBE) using NH₃. The efficiency of NH₃ as nitrogen precursor is estimated allowing the evaluation of the actual V/III ratio used during the GaN layer deposition. The growth is performed at 800-830°C under N-rich condition for growth rates larger than 1 µm/h. N- and p-type GaN layers are grown using Si and Mg solid sources, respectively. A n-type doping level up to 10¹⁹ cm⁻³ is easily achieved while p-type doping level is ranging between 1.10¹⁷ to 5.10¹⁷ cm⁻³ without needing a postgrowth annealing. GaN based light emitting diode are processed from p-n homojunctions. The growth of (Ga,In)N and (Al,Ga)N ternary alloys is also carried out. Both In and Al compositions are determined in situ by reflection high-energy electron diffraction oscillations related to bi-dimensional nucleation growth mode. Band edge versus deep level luminescence of (Ga,In)N layers will be discussed in relation with the growth conditions. The growth of (Al,Ga)N/GaN quantum wells will be also presented. Photoluminescence spectra demonstrate that MBE allows the control of the GaN well thickness at monolayer scale.
- L-V.2** 14:30-15:00 - Invited - **PROPERTIES OF CUBIC (In,Ga)N GROWN BY MBE, O. Brandt**, J.R. Müllhäuser, A. Trampert, and K.H. Ploog, Paul-Drude-Institut für Festkörperelektronik, 10117 Berlin, Germany
- Epitaxial (In,Ga)N layers form the active region of GaN-based light emitting devices. For achieving the desired blue and, particularly, green emission, high In contents are required which frequently result in bulk phase-segregation and plastic relaxation. In view of these obstacles, cubic (In,Ga)N is an interesting material since it is expected to have a significantly smaller band gap than its hexagonal relative. In fact, cubic GaN is now known to have a band gap of 3.2 eV at room temperature, which is 0.2 eV smaller than that of hexagonal GaN. We thus may expect that, at least for low In contents, the smaller band gap of cubic GaN is equivalent to an In content of about 10% "for free" when compared to hexagonal material. In this paper, we briefly review our work on thick (>100 nm) cubic (In,Ga)N layers. We find that band gaps in the blue and green spectral range are obtained with In contents of 17% and 40%, respectively, which indeed is lower than the reported values for hexagonal (In,Ga)N by at least 10%. First hints of phase separation in these thick layers are observed at an In content of 40%. In contrast, thin layers are much more well-behaving, and preliminary results indicate that the growth of cubic (In,Ga)N multiple quantum wells with only little compositional inhomogeneity is possible even at In contents above 50%.
- L-V.3** 15:00-15:20 **HIGH-SPEED GROWTH OF DEVICE-QUALITY GaN AND InGaN BY RF-MBE, K. Kushi**, H. Sasamoto, D. Sugihara, S. Nakamura, A. Kikuchi and K. Kishino, Department of Electrical and Electronics Engineering, Sophia University, 7-1 Kiou-cho, Chiyoda-ku, Tokyo 102-0094, Japan
- High-speed growth (1.2-1.4 µm/hr) of device-quality GaN epitaxial layers were demonstrated by molecular beam epitaxy using RF radical nitrogen (RF-MBE) with a room temperature (RT) PL FWHM of 31 meV and a residual carrier density of 2.7x10¹⁶ cm⁻³. Metal-insulator-semiconductor light emitting device (MIS-LED) structures with InGaN/GaN MQW active layers were grown at 1.33 µm/hr and green (567 nm) to blue (460 nm) range emission were obtained at RT under current injection.
- MBE has several superior properties to MOCVD, however the relatively low growth rate (0.2-0.8 µm/hr) makes it difficult to fabricate optical devices. In this study, we attained to 1.4 µm/hr high-speed growth of GaN by MBE using RF radical nitrogen source with high efficiency and low ionized nitrogen generation. A 4 µm thick GaN film was grown at the high growth rate on a GaN buffer layer which grown by migration enhanced epitaxy (MEE). The RT PL FWHM was 31 meV and a free exciton and a neutral donor bound exciton emission were observed at 15 K. The residual carrier density of 2.7x10¹⁶ cm⁻³ and the mobility of 159 cm²/Vs were obtained. The carrier density of Si-doped GaN films were controlled in the range from 1.7x10¹⁷ to 1.5x10¹⁸ cm⁻³ by changing a Si cell temperature. Maximum carrier density of Mg-doped p-type GaN film was 6.5x10¹⁷ cm⁻³. The growth conditions of InGaN/GaN MQW layer under the high growth rate were also investigated. The incorporation of In strongly depended on the substrate temperature, V/III ratio and In/Ga flux ratio.
- L-V.4** 15:20-15:40 **GROWTH OF ATOMICALLY SMOOTH AlN FILMS WITH A 5:4 COINCIDENCE INTERFACE ON Si(111) BY MBE, H.P.D. Schenk**, U. Kaiser, G. Kipshidze, A. Fissel, J. Kräußlich*, H. Hobert**, W. Richter, Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, *Institut für Optik und Quantenelektronik, **Institut für Physikalische Chemie, Max-Wien-Platz 1, 07743 Jena, Germany
- Epitaxial aluminum nitride films have been grown by plasma-assisted molecular beam epitaxy on Si(111). The influence of the composition of the nitrogen plasma (assessed by optical and mass spectrometry) on the crystal quality, as judged by XRD and AFM, has been investigated. Under near-stoichiometric supply of aluminum and atomic nitrogen, generated by high RF power under low nitrogen fluxes, 200 nm thick, atomically smooth films (rms-roughness=0.2 nm; 5 µm x 5 µm) have been grown at 850°C with growth rates of 2.5 µm/min. TEM investigations show that these films are homogenous 2H-AlN single crystals. Their defect structure consists of threading dislocations of mixed character mostly. The hetero-interface is abrupt and flat. Processed HRTEM images demonstrate the 5x_{AlN} to 4x_{Si} coincidence between both crystals. The FWHM of the AlN(0002)-reflex is then 0.08° in the $\theta/2\theta$ -scan and 0.6° in the ω -scan, as determined by XRD. IR spectra and derived dielectric functions hint, however, a lower degree of order compared with columnar films. Streaky RHEED-pattern hold throughout the growth and various superstructures have been observed. The $\sqrt{3}\times\sqrt{3}$ -superstructure indicates nitrogen-excess, under which irreversible column formation may occur. Layer by layer growth is generally achieved under more aluminum-rich conditions stabilizing the 6x2-superstructure instead.

SYMPOSIUM L

L-V.5 15:40-16:00

MBE GaN GROWN ON (101)NdGaO₃ SUBSTRATES, V. Mamutin, A. Toropov, N. Kartenko, S. Ivanov, A.F. Ioffe Physico-Technical Institute, St.Petersburg, Russia; **A. Wagner**, Institute of Electronic Mat. Technology, Warsaw, Poland; **P. Bergman and B. Monemar**, University of Linköping, 581 83 Linköping, Sweden

Sapphire is characterized by a large difference (16%) in the lattice parameter with GaN. Therefore, the new NdGaO₃ substrate possessing a much smaller lattice mismatch (~1%) is attractive. In this paper, we report a first successful attempt of GaN growth on NdGaO₃(101) substrates by plasma-assisted MBE. An original coaxial RF magnetron exciter is used as nitrogen source. A comparative study of epilayers grown under the same conditions on both Al₂O₃ substrates and the NdGaO₃ ones has been performed. During the GaN growth, RHEED demonstrates a streaky pattern for both types of substrates. XRD shows single-crystalline GaN structure on Al₂O₃ with the same (0001) orientation as the substrate, and the x-ray rocking curve width of the GaN (002) peak of about 1°. GaN on NdGaO₃ has the same orientation with comparable quality. The room-temperature electron concentration in GaN epilayers on both Al₂O₃ and NdGaO₃ is about 10¹⁶ cm⁻³. Time-resolved and temperature-dependent PL measurements are used to characterize the structural quality of the epilayers. The near-band-edge PL efficiency of GaN on NdGaO₃ is almost an order of magnitude higher than on Al₂O₃.

16:00-16:30

BREAK

SESSION VI - Nanostructures

Chairperson: A. Hoffmann, University of Berlin, Germany

L-VI.1 16:30-17:00 - Invited -

SELF ORGANIZATION OF NITRIDE QUANTUM DOTS BY MOLECULAR BEAM EPITAXY, B. Daudin, F. Widmann, G. Feuillet, Y. Samson, J.L. Rouvière, N. Pelekanos, Département de Recherche sur la Matière Condensée CEA-Grenoble, SP2M/PSC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Taking advantage of the Stransky-Krastanov growth mode of GaN deposited on AlN, the formation of self-organized GaN islands has been achieved in both hexagonal and cubic phases. The dots nucleation kinetics has been studied as a function of temperature and fluxes. Furthermore, various possible mechanisms allowing for size homogeneity of the dots have been investigated. In particular, dot ripening and vertical correlation effects have been shown to result in better homogeneity.

The optical properties of the GaN dots have been studied by cathodo- and photoluminescence. A blue shift is observed which is definitely assigned to quantum confinement effects, as a first step towards the realization of devices based on nitride quantum dots.

L-VI.2 17:00-17:20

GaN MICROCAVITIES AND BRAGG REFLECTORS: GIANT EXCITON LIGHT COUPLING, A. Kavokin and B. Gil, Groupe d'Etude des Semiconducteurs, CC074, Université de Montpellier II, Place Eugene Bataillon, 34095 Montpellier, France

The exciton oscillator strength in GaN exceeds one in GaAs by an order of magnitude which drastically enhances exciton-polariton effects in nitrides. Numerical simulation of light reflection from a $\lambda/2$ GaN microcavity with Ga_{0.8}Al_{0.2}N/Ga_{0.5}Al_{0.5}N Bragg mirrors revealed a record value of the vacuum-field Rabi-splitting (of the order of 50 meV). Proposed design of GaN/GaAlN Bragg mirrors tuned to the exciton resonance in GaN allows 90% modulation of the reflectivity at the exciton resonance frequency. Remarkably, both effects take place even in case of strong inhomogeneous broadening of the exciton resonance. A giant optical anisotropy of the GaN microcavities and Bragg reflectors is calculated in case of their growth on the A-plane of sapphire due to a substantial uniaxial strain. In particular, the intensity of dips in reflection spectra of the microcavity differs by a factor of 2 in two orthogonal linear polarizations of normally incident light. The calculated dispersion of exciton-polaritons in the microcavity shows in this case three modes while only two outer modes give a pronounced contribution to the spectra.

L-VI.3 17:20-17:40

FABRICATION AND PHOTOLUMINESCENCE OF GaN/SAPPHIRE NANOMETER-SCALE STRUCTURES, D. Coquillat, A. Ribayrol*, R.M. De La Rue*, S. Murad*, C. Wilkinson*, M. Julier, O. Briot, R. Aulombard, Groupe d'Etude des Semiconducteurs, UMR 5650 CNRS-Université Montpellier 2, Place Eugene Bataillon, 34095 Montpellier cedex 05, France; *Department of Electronics and Electrical Engineering, University of Glasgow, Rankine Building, Glasgow G12 8LT, Scotland, UK

We have developed a process for the fabrication of nanometer-scale structures using high resolution etching to transfer patterns from PMMA into GaN with an intermediate mask consisting of a bilayer of titanium and SiNx. Reactive ion etching in a CH₄/H₂ plasma was performed on GaN epilayers grown on (0001) sapphire. Various patterns including gratings, triangular lattices of air cylinders in GaN, triangular lattices of pillars of GaN in air, for different volume fractions of air and different periodicities have been produced. The diameter of the cylinders of air or of the pillars range from 300 nm to 1 μ m. We have investigated the photoluminescence of such patterns for the direction normal to the epilayer, in the temperature range 4.2 - 300K and at different excitation power levels, to evaluate the etch-damage. The photoluminescence from the etched structures was almost as strong as that from the unetched surface. The band gap energy and broadening parameters are determined using a lineshape analysis.

SYMPOSIUM L

L-VI.4 17:40-18:00

ON THE GAIN MECHANISM IN A NICHIA LASER DIODE, G. Mohs, T. Aoki, R. Shimano, M. Kuwata-Gonokami, Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan and S. Nakamura, Nichia Chemical Industries, Tokushima 774, Japan

We report on the gain behavior of a Nichia blue laser diode capable of cw operation at room temperature. Using optical techniques we measure modal gain spectra for various excitation powers at room temperature and compare the results to modal absorption and photoluminescence excitation spectra of the same sample.

The modal gain spectra are obtained using the variable stripe length method with nano-second excitation from a tripled, Q-switched Nd:YAG laser and show gain up to 400cm⁻¹ at 10MW/cm² pump power. Utilizing the photoluminescence of the sample as a light source and a technique similar to the variable stripe length method we also measure modal absorption spectra. Since enough optical density can be accumulated, this approach allows for unambiguous absorption measurements and the spectra clearly show the excitonic resonance of the quantum wells. This resonance is further evidenced by careful photoluminescence excitation measurements which also exhibit a clear structure close to the modal absorption peak.

The very similar spectral positions of these resonances and their vicinity to the gain maximum lead us to the conclusion that not localized excitons are responsible for the gain as suggested earlier but rather conventional two-dimensional plasma recombination.

POSTER SESSION II

Chairpersons: **W. Goetz**, Hewlett-Packard Company, San Jose, USA and **B. Daudin**, CEA Grenoble, France

18:00-20:00

See programme of this poster session p. L-27 to L-32.

Thursday June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VII -InGaN

Chairperson: S. Chichibu, University of California, Santa Barbara, USA

*also, Science University of Tokyo, Chiba, Japan

- L-VII.1** 8:30-9:00 - Invited - **INFLUENCE OF STRAIN AND BUFFER LAYER TYPE ON In-INCORPORATION DURING GaInN MOVPE**, F. Scholz, J. Off, A. Kniest, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany; O. Ambacher, Walter-Schottky-Institut, TU München, 85748 München, Germany
GaInN/GaN hetero structures play a key role for optoelectronic devices emitting light in the visible and near UV spectral region. However, the incorporation of In during the epitaxy of GaInN is low and depends on many critical parameters as temperature, carrier gas type, growth rate etc. Moreover, the layers on which the GaInN is grown obviously influence the In incorporation and the quality of the grown films. Therefore we have studied the low pressure metalorganic vapor phase epitaxial growth of GaInN layers on different types of buffer layers. We found that not only the type of the buffer layer material (e.g. GaN or AlN) but also its thickness influences the In incorporation, indicating that strain and lattice mismatch play a key role in the observed behaviour. Relaxed layers grown directly on the sapphire substrate show a higher In content than those grown pseudomorphically strained on GaN buffer layers. These phenomena have been studied by analyzing the strain by high resolution x-ray diffraction and the opto-electronic properties by photoluminescence and photothermal deflection spectroscopy. Moreover, first attempts have been done to control the strain by growing quaternary AlGaInN layers.
- L-VII.2** 9:00-9:20 **COMPOSITIONAL INHOMOGENEITIES IN InGaN STUDIED BY TRANSMISSION ELECTRON MICROSCOPY AND SPATIALLY RESOLVED CATHODOLUMINESCENCE**, H. Selke, T. Böttcher, S. Einfeldt, D. Hommel, P.L. Ryder, University of Bremen, PO Box 330440, 28334 Bremen, Germany; F. Bertram and J. Christen, University of Magdeburg, PO Box 4120, 39106 Magdeburg, Germany
The structural and optical properties of InGaN epilayers and InGaN/GaN heterostructures grown by conventional or modulated beam molecular beam epitaxy (MBE) on basal plane sapphire were studied by analytical transmission electron microscopy (TEM), energy-dispersive x-ray microanalysis (EDX), high-resolution TEM and spatially resolved cathodoluminescence (CL). Mappings of the local emission wavelength obtained by spatially resolved CL indicate inhomogeneities in the chemical composition of InGaN epilayers grown by conventional techniques. These results agree well with mappings of the indium to gallium ratio obtained by EDX in TEM. The overall indium concentration decreases slowly in the growth direction, but there is a thin indium-rich surface layer. The lateral variations in indium concentration are irregular and more pronounced. These findings are consistent with the growth model proposed by Schetzina et al.. Epilayers grown by the modulated beam MBE technique are more homogeneous in the lateral and in the growth direction. No indium-rich surface layer is present in these samples. In addition InGaN/GaN quantum well structures are at present under investigation. Latest results will be presented.
- L-VII.3** 9:20-9:40 **LARGE AND COMPOSITION-DEPENDENT BAND-GAP BOWING IN $\text{In}_x\text{Ga}_{1-x}\text{N}$ ALLOYS**, C.G. Van de Walle, M.D. McCluskey, C.P. Master, L.T. Romano, and N.M. Johnson, Xerox PARC, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA
We show that the band gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ exhibits significantly larger bowing than has been commonly assumed. In addition, the bowing is strongly composition dependent. Our first-principles calculations, based on pseudopotential-density-functional theory, produce values of the bowing parameter b_b equal to 4.8, 3.5, and 3.0 eV, for $x=0.0625$, 0.125, and 0.25 respectively. These results agree with an analysis of optical-transmission spectroscopy measurements on $\text{In}_x\text{Ga}_{1-x}\text{N}$ epilayers. Using x-ray diffraction (XRD) and Rutherford backscattering spectrometry these layers were determined to be pseudomorphically strained. Properly including the effects of strain on the band structure is essential: ignoring strain can lead to an overestimation of the In content based on XRD. This misinterpretation may explain previous experiments that have yielded a bowing parameter of $b_b \approx 15 \text{ eV} \cdot \text{Å}^2$. The band-gap values derived here eliminate the need for invoking the presence of deep levels or large composition fluctuations to explain deviations between measured transition energies and the previously commonly accepted band gap. S. Nakamura, Solid State Commun. (b102), 237 (1997).
- L-VII.4** 9:40-10:00 **THE COMPOSITION PULLING EFFECT IN THE MOVPE GROWTH OF InGaN/GaN HETEROSTRUCTURES** M. Schwambra, O. Schoen, D. Schmitz, M. Deschler, M. Heuken, AIXTRON AG, Kackertstr. 15-17, 52072 Aachen, Germany; B. Schineller, Institut für Halbleitertechnik, RWTH Aachen, Templergraben 55, 52056 Aachen, Germany
We investigated GaInN/GaN heterostructures for blue light emitters grown with an AIX 200 RF MOVPE system. We investigated the dependence of InGaN growth on deposition temperature and In/(In+Ga) gas phase ratio. The dependence of the optical, electrical and structural properties were characterized by XRD, RT and LT PL, SIMS and electrical measurements. For different In/(In+Ga) gas phase ratios we found a decreasing In incorporation with increasing growth temperature. LT PL measurements indicate that with higher growth temperature one can achieve better optical quality (lower FWHM of peaks) of the GaInN films. XRD measurements indicate that the In incorporation is getting less dependent on growth temperature and gas phase composition with increasing the temperature due to In desorption. The composition pulling effect causes an increasing In content with layer thickness shown by SIMS which causes discrepancies between PL and X-ray measurements for the evaluation of the In composition. We achieved a very good compositional homogeneity (proved by PL mapping) of the grown films with a standard deviation of 1.11 nm.

10:00-10:30

BREAK

SESSION VIII - Characterization

Chairperson: D. Hommel, University of Bremen, Germany

- L-VIII.1 10:30-11:00 - Invited -** **III-V NITRIDE MATERIALS FOR HIGH EFFICIENCY VISIBLE LIGHT EMITTING DIODES**, W. Goetz, Hewlett-Packard Company, Optoelectronics Division, 370 West Trimble Road, San Jose CA 95131, USA
The fabrication and optimization of devices based on III-V nitrides (AlGa_xN, InGa_xN, and GaN) is driven by advancements in materials technology. Control and optimization of the doping is one of the keys to improve device performance.
In my talk I will report on electrical characterization of dopants for GaN and Al_xGa_{1-x}N ($x < 0.12$). Variable temperature Hall-effect measurements were employed to derive parameters for shallow dopants. Among the donors investigated were SiGa, ON, and GeGa. These donors introduce shallow levels into the bandgap of GaN near the conduction band edge. The Mg acceptor (MgGa) is the shallowest acceptors known for doping III-V nitrides p-type despite an activation energy for thermal ionization of ~150 meV. For AlGa_xN the ionization energy rapidly increases as the Al composition increases. Hall-effect measurements of III-V nitrides are often complicated by the presence of conducting interfacial layers, which were taken into account.
Optimization of n- and p-type III-V nitride layers has permitted the fabrication of high performance visible LEDs. For example, for LEDs emitting at ~500 nm, external quantum efficiencies >10 % and forward voltages of ~3.1 V at 20 mA were accomplished. These diodes exhibit excellent reliability and long life.
- L-VIII.2 11:00-11:20** **CHARACTERIZATION OF OPTICAL INDUCED DEFECT-BAND-TRANSITIONS IN MBE GROWN GALLIUMNITRIDE BY OPTICAL ADMITTANCE SPECTROSCOPY**, A. Krtschil, M. Lisker, H. Witte, J. Christen, Institute of Experimental Physics, University of Magdeburg, PO Box 4120, 39016 Magdeburg, Germany and U. Birkle, S. Einfeldt, D. Hommel, Institute of Solid State Physics, University of Bremen, PO Box 330, 28334 Bremen, Germany
Optical induced transitions between states in the gap and the corresponding band in GaN were analyzed by Optical Admittance Spectroscopy (OAS) in the temperature range from 20K to 300K and for modulation frequencies between 50mHz and 1MHz. The various contributions of the broad bands, e.g. near the band edge, were separated using their temperature- and excitation dependence. The spectral photoionization cross section of deep levels in GaN was measured for the first time. The samples investigated were grown by MBE on (0001) Sapphire.
The transitions in OAS are classified into three different spectral regions:
1.) A broad band consisting of at least two peaks at 50meV and 160meV below EG following the temperature dependence of EG.
2.) Midgap states appear at photon energies between 1.5eV and 2.5eV where commonly the yellow luminescence band is visible in PL. A strong dependence of relative contributions on excitation conditions is observed (memory effect). The individual peak positions are independent of temperature.
3.) Sharp peaks due to deep level band transitions at 0.82eV and 1.27eV were found and from the dependence of the peak position on the modulation frequency we calculated the spectral photoionization cross section. As example, the cross section of the trap at 0.82eV was evaluated between 10-17cm² and 10-9cm² as function of the photon energy.
- L-VIII.3 11:20-11:40** **EXAFS STUDIES OF GROUP III-NITRIDE ALLOY SEMICONDUCTORS**, A.V. Blant, N.J. Jeffs, T.S. Cheng, Department of Physics, University of Nottingham, Nottingham NG2 7RD, UK; C. Bailey, P.G. Harrison, Department of Chemistry, University of Nottingham, Nottingham NG2 7RD, UK and J.F.W. Mosselmans and A.D. Smith, CLCR Daresbury Laboratories, Warrington, Cheshire, WA4 4AD, UK
The Group III-Nitrides are currently being used extensively for visible light emitting diodes and FETs (and will form the basis of blue/UV lasers) and in each case the active part of the device consists of an (InGa)N alloy, with other parts of the device structure using (AlGa)N. In the Group III-Nitride alloys there is a considerable mis-match in lattice parameter between the binary end members, this in turn leads potentially to spinodal decomposition. EXAFS studies provide unique information about the local environment and bond lengths in materials and we have undertaken a study of Group III-Nitride alloys using this technique. The samples used in this study were grown by a nitrogen plasma-assisted molecular beam epitaxy (PA-MBE), with all other elements provided by conventional Knudsen cells. A range of samples from InN through GaN to AlN have all been prepared at low temperatures (400°C) which should kinetically hinder spinodal decomposition. In our initial (InGa)N study, using EXAFS at the In Edge, the samples showed alloy formation. Here we will discuss for the first time data obtained for (AlGa)N from the Al edge.
- L-VIII.4 11:40-12:00** **PROBING THE LOCAL DIELECTRIC/OPTICAL PROPERTIES OF GROUP III-NITRIDES BY SPATIALLY RESOLVED EELS ON THE NANOMETER SCALE**, G. Brockett, and H. Lakner, Gerhard-Mercator-Universität Duisburg, Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany
Usually, information on the dielectric-optical properties of semiconductors is obtained from spectroscopic ellipsometry. In order to cover the necessary spectral range between 2 and 25 eV synchrotron radiation must be used. But such measurements lack of spatial resolution. In this work the local electronic structure of (In, Ga, Al)N heterostructures has been investigated by electron energy loss spectroscopy (EELS). The used cold field-emission scanning transmission electron microscope (VG HB501) was equipped with a dedicated parallel EELS-system (0.4 eV resolution). Using subnanometer electron probes the spatial resolution of the measurements depends on the physical localization of the scattering process itself. Thus the spatial resolution of low-loss EELS is in the range of 10 nm while the transitions in the core-loss region can be observed on a sub-nanometer scale.
The low-loss region of the energy spectra reveals information on plasmon excitations and transitions across the band gap and the characteristic shape of the joint density of states. From these results the local dielectric/optical properties can be deduced via a Kramers-Kronig transformation. Furthermore, investigations on the core-loss region of the EEL-spectra show significant changes in the characteristic structure of the N-K-edge within the individual (In, Ga, Al)N layers. The results obtained are in excellent agreement with theoretical studies and ellipsometry measurements.

SYMPOSIUM L

L-VIII.5 12:00-12:20

RAMAN SPECTROSCOPY OF DISORDER EFFECTS IN AlGa_xN SOLID SOLUTIONS, V.Yu. Davydov, I.N. Goncharuk, M.V. Baidakova, and A.N. Smirnov, Ioffe Physicotechnical Institute, 194021 St.Petersburg, Russia; A.V. Subashiev, State Technical University, 195251 St.Petersburg, Russia; J. Aderhold, J. Stemmer, D. Uffmann, and O. Semchinova, Lfi Universität Hannover, 30167 Hannover, Germany
We report the results of the experimental and theoretical studies of the disorder effects in the hexagonal Al_xGa_{1-x}N epitaxial layers grown by MBE and HVPE for a large range of Al concentrations, from GaN to AlN. The basic experimental technique was Raman spectroscopy, but some data were obtained in X-ray and AFM studies. The abnormally small broadening of the A₁(TO) polar phonon mode for $x(1-x) < 0.25$ and a large broadening for x close to 0.5 are attributed to the specific frequency dependence of the density of states for the branch with the directional dispersion in pure crystals. This interpretation is consistent with the observed anisotropy of the line width as a function of the phonon propagation direction in a mixed crystal. The width of the nonpolar phonon line with symmetry E₂ is caused by phonon scattering on the Al content spatial fluctuations and is found to be proportional to $x(1-x)$. Thus Raman spectrum of these lines is highly sensitive to the mixed crystal composition and its inhomogeneity.

12:20-14:00

LUNCH

Thursday June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-Midi

SESSION IX - LED-LASER

Chairperson: A. Hangleiter, University of Stuttgart, Germany

- L-IX.1** 14:00-14:30 - Invited - MOCVD GROWTH AND CHARACTERIZATION OF AlGaInN HETEROSTRUCTURES AND LASER DIODES, **D.P. Bour**, M. Kneissl, W.M. Johnson, L. Romano, B.S. Krusor, M. McCluskey, J. Walker and R.D. Bringans, Electronic Materials Laboratory, XEROX Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto CA 94304, USA
GaN and InGaN/AlGaIn heterostructures have been deposited on A- and C-face sapphire substrates by MOCVD. We describe the structural and optoelectronic properties of these materials, and the performance characteristics of LEDs and laser diodes. Room temperature, pulsed operation of a violet laser diode ($\lambda = 420$ nm), containing $10 \times 20 \text{ Å}$ $\text{In}_{0.2}\text{Ga}_{0.8}$ N/GaN and $\text{Al}_{0.08}\text{Ga}_{0.92}$ N cladding layers, was obtained, with threshold current density 20 kA/cm^2 .
- L-IX.2** 14:30-15:00 - Invited - GAN LATERAL EPITAXIAL OVERGROWTH AND DEVICES, **S.P. DenBaars**, H. Marchand, P. Fini, J. Ibbetson, P. Kozodoy, J. Speck, and U. Mishra, Materials Department, Univ. California, Santa Barbara CA 93106, USA
Extended defect reduction at the surface of GaN grown by lateral epitaxial overgrowth (LEO) on large-area GaN/Al₂O₃ wafers by low pressure MOCVD is verified by atomic force microscopy and TEM. GaN grown vertically through the mask openings (windows) retains a high TD density; however material which then grows laterally across the mask has a drastically reduced TD density. This recent has shown a reduction in TD density from $\sim 4 \times 10^8 \text{ cm}^{-2}$ in the window region to below 10^5 cm^{-2} in the LEO region. The density of mixed character threading dislocations at the surface of the LEO GaN is reduced by at least 3-4 orders of magnitude from that of bulk GaN. Simple p-n diode devices were fabricated on LEO material and electrical characteristics of GaN p-n junctions has been examined through current-voltage measurements. A comparison of p-n diodes fabricated in each region reveals that reverse-bias leakage current is reduced by over four orders of magnitude on LEO GaN.
- L-IX.3** 15:00-15:20 GaN-BASED LASER DIODE WITH FOCUSED ION BEAM-ETCHED MIRRORS, **C. Anbe**, T. Takeuchi, R. Mizumoto, H. Katoh, S. Yamaguchi, C. Wetzel, H. Amano and I. Akasaki, Department of Electrical and Electronic Engineering, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan and Y. Kaneko and N. Yamada, Hewlett-Packard Laboratories, 3-2-2 Sakado, Takatsu-ku, Kawasaki 213-0012, Japan
MQWs-SCH LD structure was grown on a sapphire (0001) substrate by OMVPE. It consists of GaN optical waveguide layer, AlGaIn cladding layer, and active layer which consists of five pairs of $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}$ well 2 nm thick and $\text{Ga}_{0.97}\text{In}_{0.03}\text{N}$ barrier 4 nm thick. $5 \mu\text{m}$ wide ridge was formed by chlorine based RIE. Cavity length is $500 \mu\text{m}$. After cleaving the wafer along the (1100) plane of the sapphire, FIB etching was done for both cleaved side edges with a focused Ga^+ ion beam accelerated at 30 kV and beam current of 130 pA. AFM image shows RMS roughness of FIB-etched side mirrors are 0.6 nm. It shows lasing by pulsed current injection at room temperature. Threshold current and the lasing wavelength are 0.75 A and around 410 nm, respectively. To the best of our knowledge, this is the first demonstration of the GaN-based laser diode with Fabry-Perot resonator mirrors fabricated by FIB etching.
- L-IX.4** 15:20-15:40 FABRICATION AND CHARACTERIZATION OF GaN/InGaN/AlGaIn DOUBLE HETEROSTRUCTURE LEDs AND THEIR APPLICATION IN LUMINESCENCE CONVERSION LEDs (LUCOLEDS), **P. Schlöter**, J. Baur, Ch. Hielscher, M. Kunzer, H. Obloh, R. Schmidt, J. Schneider, Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, 79108 Freiburg, Germany
We report on the fabrication as well as on the optical and electrical characterization of violet, blue and green emitting GaN/InGaN/AlGaIn double heterostructure LEDs covering the 385nm-550nm spectral range. MOCVD grown epitaxial layer sequences were processed into mesa diodes by chemically assisted ion-beam etching and contact metallization. To achieve packaged LED devices the diode chips were encapsulated in transparent epoxy resin using standard technology. Based on the blue emitting diodes as primary light sources white luminescence conversion LEDs (LUCOLEDS) have been fabricated. Using commercially available perylene dyes or YAG:Ce phosphors as the luminescent material, the LED radiation is converted into light of longer wavelengths by luminescence down-conversion (Stokes shift). In contrast to conventional LEDs which only emit quasi-monochromatic light, light of nearly all colors can be generated by this technique. By mixing the primary blue light with the radiation emitted from the converting material also white and mixed colors have been generated.

SYMPOSIUM L

L-IX.5 15:40-16:00

GaN_{0.9}N-DFB-LASERS WITH OVERGROWN DFB-GRATINGS, R. Hofmann, M. Neuner, J. Off, F. Scholz, H. Schweizer, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

We report on GaInN distributed-feedback (DFB) lasers with a separate confinement heterostructure (SCH), which were accomplished by overgrowing etched DFB-gratings. Laser emission around 410 nm was observed by optical pumping of the overgrown DFB-lasers at room temperature. The successful embedding of the DFB-gratings is one step towards electrically pumped GaN-DFB-lasers.

To realize the SCH-DFB lasers the n-side AlGaIn cladding, the lower GaN waveguide, the GaInN active layer, and the upper GaN wave-guide were grown first by MOVPE using SiC substrates. The gratings were then defined by e-beam lithography and transferred into the upper GaN waveguide by ECR-RIE dry etching. In a second epitaxial step, also MOVPE, the laser structure was completed by growing the upper AlGaIn cladding layer. Finally, a mesa was etched to provide lateral waveguiding.

Optically pumped, the lasers show a clear threshold behaviour. The spectral position of the laser emission of the overgrown GaInN-DFB-lasers shows the typical dependence on the grating period. By varying the grating period, laser emission between 402 nm and 421 nm was achieved. In this spectral range the effective refractive index of the SCH structure and its dispersion was determined.

16:00-16:30

BREAK

SESSION X - AlGaIn/GaN

Chairperson: K.P. O'Donnell, University of Strathclyde, Scotland

L-X.1 16:30-17:00 - Invited -

OPTICAL PROPERTIES AND LASING OF GaN/Al_xGa_{1-x}N QUANTUM WELLS, L. Calcagnile, G. Coli', M. Lomascio, and R. Cingolani, Istituto Nazionale per la Fisica della Materia, Dipartimento di Scienza dei Materiali, Università di Lecce, 73100 Lecce, Italy; H. Tang, A. Botchkarev, W. Kim, A. Salvador, and H. Morcoç, Coordinated Science Laboratory and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana-Champaign Urbana, Illinois 61801, USA

GaN and its alloys have been receiving an enormous attention for their physical properties which make them useful for the realisation of high temperature and high power electronic devices. By a proper choice of alloy concentration the emitted radiation can be tuned from the visible into the ultraviolet. In this work we investigated a set of GaN/Al_xGa_{1-x}N separate confinement quantum well structures with well width from 2 to 5 nm deposited by reactive molecular beam epitaxy on c-plane sapphire substrates. Optical properties as a function of well width, temperature, excitation intensity, were investigated by photoluminescence, photoluminescence excitation, and magnetoluminescence up to 8 T. Samples exhibited stimulated emission up to room temperature with threshold close to 40 kW/cm². The mechanism of exciton localisation and their impact on lasing and emission spectra will be discussed in detail.

L-X.2 17:00-17:20

MICROCALORIMETRIC ABSORPTION SPECTROSCOPY IN GAN ALGAN QUANTUM WELLS, A. Göldner and A. Hoffmann, Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany; B. Gil and P. Lefebvre, Groupe d'Etude des Semiconducteurs, CC074, Université de Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France; P. Bigenwald and Ph. Christol, Université d'Avignon et des Pays de Vaucluse, Boulevard Pasteur, 84000 Avignon, France; H. Morkoç, Virginia Commonwealth University, 921 West Franklin Street, P.O. Box 843072, Richmond Virginia 23284-3072, USA

Micro-calorimetric measurements of small absorption coefficients have been performed on thin GaN-AlGaIn quantum wells grown by Molecular Beam Epitaxy on Al₂O₃ substrates. In addition to strong absorption at the energy of the GaN buffer and at the energy of the thick AlGaIn barrier layers, we could also readily detect, both fundamental and excited transitions associated to the quantum well. These measurements which furnish precise determination of the gap mismatch between the well and the barrier layers are combined with self consistent excitonic and envelope function calculations in the context of a model for the band line-ups which include built-in piezo-electric fields. We find the transition energies and the oscillator strengths to be in excellent agreement with the experiment.

L-X.3 17:20-17:40

CHARGE CONTROL SIMULATION AND EXPERIMENTAL MEASUREMENT OF TRANSFER CHARACTERISTICS OF AlGaIn/GaN HEMTs, M.S. Krishnan, A. Dimoulas and A. Christou, University of Maryland, College Park, MD 20742-2115, USA

Conventional high electron mobility transistors (HEMTs) based on AlGaIn/GaN heterostructures have been accurately modeled and the results are described in this paper. The Schrodinger's equation and the Poisson's equation have been solved self-consistently in order to obtain a relationship between the sheet carrier density and the applied gate voltage. The relationship is treated using a non-linear exponential fit that enables a more accurate analysis of the saturation region compared to other models used hitherto. The I-V characteristics have then been predicted by a charge control analysis that utilizes the exponential charge-potential relationship which helps exactly identify the saturation point without having to resort to parameter extraction from other experiments. This leads to separating the linear and saturation regions by a well defined boundary as a result of which the I-V characteristics are more accurately modeled. The intrinsic non-linearity also helps in explaining why the devices do not pinch off to one value. HEMTs based on AlGaIn/GaN have been fabricated on semi-insulating GaAs substrates where the GaN layer was grown by pulsed laser deposition and the AlGaIn by VPE techniques. Drain current saturation was obtained for gate voltage from -1.5 to -3.5 volts in agreement with the simulation results.

L-X.4 17:40-18:10 - Invited -

RECOMBINATION DYNAMICS OF EXCITONS IN III-NITRIDE LAYERS AND QUANTUM WELLS, P. Lefebvre, Groupe d'Etude des Semiconducteurs, CNRS, Université Montpellier II, CC 074, 34095 Montpellier cedex 5, France

A comparison of the various aspects of current research on exciton dynamics in GaN-based epitaxial layers is proposed. To date, most contributions have been concerned by: 1) micrometric epitaxial layers of GaN, the physics of which essentially deals with the identification and control of non-radiative processes; 2) InGaN/GaN multiple quantum wells, for which several hypotheses are currently competing for explaining the very long decay times observed, related to strong localization effects.

By a review of current literature and of our recent research, it is shown that the temporal behavior of radiative recombinations in these systems is ruled by a number of hardly controlled factors, whereas the physics of low-dimensional excitons in GaN/GaAlN quantum wells is quite similar to that in the model system GaAs/GaAlAs, developed in the past decade. Measurements of the decay times of free and localized excitons in GaN / GaAlN quantum wells, versus temperature T , are presented. The radiative lifetime of free excitons varies linearly with T , in agreement with available theories on bidimensional excitonic polaritons. The low-temperature limit of this lifetime is deduced to be much smaller than in GaAs/GaAlAs quantum wells, and consistent with a longitudinal-transverse splitting of 0.6 meV. The theoretical analysis of relative decay times of free excitons and localized states indicate that the latter correspond to electrons and holes having localization radii smaller than the Bohr radius.

Friday June 19, 1998
Vendredi 19 juin 1998

Morning
Matin

SESSION XI - Growth: ELOG

Chairperson: F.A. Ponce, Xerox Parc, Palo Alto, USA

- L-XI.1** 8:30-9:00 - Invited - **SELECTIVE AREA GROWTH AND EPITAXIALLY LATERAL OVERGROWTH OF GaN BY MOVPE AND HVPE, K. Hiramatsu**, Mie University, Dept of Electrical & Electronic Eng, 1515 Kamihama, Tsu 514-5807, Japan
The selective area growth (SAG) of III-V nitride semiconductors is a promising technique not only for fabricating electronic or optical device structures but also for realizing dislocation-free substrate using the epitaxially lateral overgrowth (ELO). In this paper, we report recent successful results on the SAG and ELO of GaN that has been done by MOVPE and HVPE. Both the growths were carried out on MOVPE-grown GaN (0001) / sapphire substrates with lined or dotted SiO₂ masks.
Sub-micron GaN dot and line structures were fabricated by the SAG in MOVPE and also buried structures of the SiO₂ submicron lines were realized using the ELO technique. The buried structures were confirmed to have smooth surfaces and no grain boundaries. The reduction in dislocation density was confirmed using TEM and a growth pit density (GPD) technique in InGa_{0.5}N on the ELO GaN layer.
Furthermore, thick GaN bulk single crystals without any cracks were obtained using the SAG in HVPE. Crystalline and optical properties of the GaN bulk were much improved. The defect structures were also characterized by GPD and TEM techniques. The reduction in the thermal strain due to the growth on the limited area as well as the ELO on the mask area were found to be effective to reduce crystalline defects of the GaN bulk single crystals.
- L-XI.2** 9:00-9:20 **EPITAXIAL LATERAL OVERGROWTH GaN STRUCTURES - SPATIALLY RESOLVED CHARACTERIZATION BY CATHODOLUMINESCENCE MICROSCOPY AND MICRO-RAMAN-SPECTROSCOPY, F. Bertram**, T. Riemann, J. Christen, Otto-von-Guericke-Universität Magdeburg, PO Box 4120, 39016 Magdeburg, Germany; H. Siegle, A. Hoffmann, Technische Universität Berlin, Germany, K. Hiramatsu, Mie University, Mie, Japan
Epitaxial lateral overgrowth (ELO) GaN structures are comprehensively microcharacterized by scanning cathodoluminescence microscopy (CL) and micro-Raman-spectroscopy (μ -Raman). Following an AlN-buffer, a 2 μ m thick GaN-epilayer is grown by MOVPE on (0001) sapphire and subsequently structured using a SiO₂-mask. Finally, the resulting stripe pattern is overgrown with HVPE-GaN. Various mask geometries, i.e. stripe width/thickness and lateral spacing, their orientation in $\langle 1120 \rangle$ - and $\langle 1100 \rangle$ -direction, respectively, as well as various overgrowth schemes are investigated. CL-microscopy directly visualizes the striking differences between the coherent grown regions (between the SiO₂-stripes) and the overgrown areas. The overgrown GaN shows a strong blue-shift and broadening of the luminescence, while the CL from the coherent areas is dominated by the strain-shift narrow (D₀,X)-emission. This indicates a strong impurity (Si- or O-donors) incorporation into the overgrowth GaN on the top of the SiO₂-stripes. This interpretation is strongly confirmed by μ -Raman, proving that the blue-shifted ELOG-GaN on top of the SiO₂ is completely unstrained, whereas a strain gradient is measured on the coherently grown GaN between the SiO₂-stripes.
- L-XI.3** 9:20-9:40 **LATERAL EPITAXY PHENOMENON AND DISLOCATION DENSITY REDUCTION IN SELECTIVELY GROWN GaN STRUCTURES, T.S. Zheleva**, Ok-Hyun Nam, W.M. Ashmawi*, and R.F. Davis, Department of Materials Science and Engineering, North Carolina State University, *Department of Mechanical Engineering, Raleigh, NC 27695, USA
The studies represent a comparison between the structural quality at different regions of GaN films grown selectively within windows in SiO₂ deposited on GaN/AlN/6H-SiC heterostructures. The MOVPE grown GaN structures - hexagonal pyramids, stripes or continuous films, are epitaxial and single crystalline. However, there are two distinct regions exhibiting significantly different crystal structure quality in these GaN structures. The regions of GaN grown selectively and vertically above the SiO₂ window areas exhibit the usual defect density of 10⁸-10¹⁰ cm⁻². These defects are predominantly threading dislocations with dislocation lines nearly vertical or vertical with respect to the interfacial planes i.e. of mostly mixed character: with Burgers vector $b=1/3\langle 1123 \rangle$ and also edge dislocations with burgers vector $b=1/3\langle 1120 \rangle$. The regions of GaN which overgrow laterally the SiO₂, or the regions of lateral epitaxial overgrowth (LEO-GaN), are nearly defect free with dislocation density less than 10⁴ cm⁻². The usual defects in these regions are short dislocations segments with lines parallel to the interfacial planes which usually are aligned parallel or nearly parallel to the [1100] or [1120] directions, depending on the orientation of the SiO₂ stripe, along [1120] or along [1100] direction, respectively. This effect of four-to-six orders of magnitude reduction in the dislocation density in LEO-GaN is associated with the lateral epitaxy phenomenon i.e. change of the growth direction of the selectively grown GaN. This change of the growth direction is related with a different mechanism of formation of the facets participating in the vertical or the lateral growth - {0001}, or {1120}, {1100} and {1101}, respectively. A finite element analysis (FEA) reveals that a major mechanism that enables such distinct periodic appearance of regions with very low density of dislocations is the accommodation of the thermal mismatch existing among the different phases in the heterostructures.

SYMPOSIUM L

L-XI.4 9:40-10:00

HIGH QUALITY LOG-GaN LAYERS ON GaN/Al₂O₃ PATTERNED SUBSTRATES BY HALIDE VAPOUR PHASE EPITAXY, G. Nataf, B. Beaumont, A. Bouillé, P. Vennéguès, S. Haffouz, M. Vaille and P. Gibart, Centre de Recherche sur l'Hétéroépitaxie et ses Applications (CRHEA-CNRS), Rue B. Gregory, Sophia Antipolis, 06560 Valbonne, France

The growth and characterisation of thick GaN layers by Halide Vapour Phase Epitaxy (HVPE) on patterned MetalOrganics Vapour Phase Epitaxy (MOVPE)-GaN/Al₂O₃ substrates is reported. The growth on small area features has shown that lateral overgrowth was enhanced following preferential crystallographic directions. Double Crystal X-Ray Diffraction (DCXRD) assessment in ω scan showed 50 arcsec Full Width at Half Maximum (FWHM) for layers grown on a small area hexagonal holes field.

On the way towards the realisation of self-supported GaN substrates, the present study was extended to Epitaxial Lateral Overgrowth (ELOG) on large surface GaN/Al₂O₃ patterned substrates to achieve coalescence. Hexagonal holes and parallel stripes features were used. Structural, electrical and optical characterisation of such layers was performed, underlining the promising quality of these materials.

10:00-10:30

BREAK

SESSION XII - Process and Device

Chairperson: K. Kishino, Sophia University, Tokyo, Japan

L-XII.1 10:30-11:00

- Invited -

A. Riechert, Siemens, Germany

L-XII.2 11:00-11:20

NOVEL PLASMA CHEMISTRIES FOR HIGHLY SELECTIVE DRY ETCHING OF In_xGaN_{1-x}, BI₃ AND BBr₃, H. Cho, J. Hong, T. Maeda, S.M. Donovan, C.R. Abernathy, S.J. Pearton, Department of Materials Science and Engineering, University of Florida, Gainesville FL 32611, USA and R.J. Shul, Sandia National Laboratories, Albuquerque, NM 87185, USA

There is increasing need for dry etch chemistries with high selectivity for one nitride over another. Our previous work has shown that C12/Ar Inductively Coupled Plasmas can produce selectivities >8:1 for GaN:AlN and ~6.5:1 for GaN:InN under optimized conditions. In high power nitride-based electronic devices, selective removal of InN or InGaIn contact layers in HEMTs or HFETs, or of base layers in HBTs under low damage conditions is necessary. Two new plasma chemistries, BI₃ and BBr₃ are found to produce selectivities >10:1 for InN and InGaIn over GaN and AlN in ICP discharges, due to the relatively high volatility of InI₃ and InBr₃ etch products. Etch rates >5,000 Å/min for InN are obtained at high source and rf chuck powers. Both reactants are readily dissociated in the ICP source, as evidenced by the strong atomic transitions in optical emission spectra. Surface morphology of the etched nitrides is found to depend on plasma composition, chuck power and source power, but root-mean-square roughness similar to the as-grown material are obtained over a wide range of etching conditions.

L-XII.3 11:20-11:40

EFFECT OF As DIFFUSION ON P-TYPE GaN CONTACTS, S. Uchida, D. Cohen, A. Abare, J. Ko, R. Naone, B. Mason, E. Hegblom, Y. Akulova, P. Kozody, U. Mishra, L.A. Coldren, S.P. DenBaars, University of California, Santa Barbara CA 93106, USA
The effect of As diffusion on the contacts to Mg-doped GaN was investigated. It was found that As diffusion into p-GaN reduced the contact resistance and the Schottky barrier height. As was diffused into a p-GaN layer by three methods; 1) Contact diffusion between two wafers, one p-GaN and the other Be-doped GaAs; 2) Diffusion from an Arsenosilica film which contains 2-3% As; 3) Diffusion from a 7.5nm layer of As atoms deposited by MBE. Before the As diffusion, p-GaN samples were annealed at 660°C for 30 minutes in order to activate the Mg. All diffusion processes were done by annealing at a temperature of 900-1045°C in nitrogen gas. After the As diffusion, Ni/Au was evaporated as a p-type ohmic metal.
The lowest contact resistivity, 3.7x 10⁻³ (ohm-cm²), was obtained by Contact As diffusion at 927°C annealing for 60 minutes. We found that lower temperatures and longer diffusion times are much more effective at reducing the contact resistance.

L-XII.4 11:40-12:00

THE ANALYSIS OF CONTACT RESISTIVITY BETWEEN A P-TYPE GaN LAYER AND ELECTRODE IN InGaIn MQW LASER DIODES, M. Onomura, S. Saito, L. Sugiura, M. Nakasuji, K. Sasanuma, J. Nishio, J. Rennie, Shin-ya Nunoue, and K. Itaya, Toshiba Corp., Advanced Semiconductor Devices Laboratories, Kawasaki 210-8582, Japan

The reduction of the operation voltage is important for realization of long lifetime and high output power operation of InGaIn MQW laser diodes (LDs). On studying the separate individual elements contributing to the excess voltage drop in the LDs, we were able to conclude the following.

The specific contact resistivity (ρ_c) to p-GaN was estimated by transmission line model (TLM) method and was estimated to slightly vary from 1 x 10⁻³ to 6 x 10⁻⁴ Ωcm² in the current range of 1 to 10 kA/cm². This result is low in comparison to the previous reports, because of the lack of given data in the range of the threshold current density required for lasing. It is found that an Ohmic-like contact was obtained by optimizing both the acceptor density of p-GaN and the contact metals.

The respective voltage drop at the p-side contact in our LDs was found to be 5.6 V for a device with a threshold current density of 6.7 kA/cm² (I_{th} = 100 mA) at 14 V under R.T. pulsed operation. The remaining excess voltage drop was thought to be derived from the series resistance and the built in potential of MQW. It is found that the excess voltage drop in these devices is mainly due to the p-side contact resistance.

SYMPOSIUM L

L-XII.5 12:00-12:20

W AND W/WSi_y/In_{1-x}Al_xN OHMIC CONTACTS TO GaN, A. Zeitouny, M. Eizenberg, Dept. of Materials Engineering, Technion - Israel Institute of Technology, Haifa 32000, Israel; S.J. Pearton, Dept. of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA; F. Ren, Dept. of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

GaN is a good candidate for high temperature and high power devices. In order to obtain good stable ohmic contacts, two approaches are currently being investigated. In the first one, the ohmic contact is enabled by forming a highly n⁺ region by Si implantation. In the second approach, a graded In_{1-x}Al_xN epilayer will facilitate the proper band alignment needed for an ohmic contact. The thermal stability of the metallization for both approaches is guaranteed by using W and WSi.

In the first approach 1000Å of W have been deposited on 3µm of Si implanted (5-10¹⁵cm⁻³, 100 KeV, 1150°C/10 sec activated) n⁺ GaN (n>10²⁰cm⁻³) grown on Sapphire. The samples were RTA treated at 750, 850, 950 and 1050°C for 10sec. The 750, 950 and 1050°C anneals produced good ohmic contacts with specific resistivities ranging from 1.1·10⁻⁴ to 2.6·10⁻⁶ Ωcm² as measured by the TLM technique. The large spread in resistivities is yet unexplained but is consistent with other data published for GaN. XRD or AES detected no compound formation.

In order to test the feasibility of the second approach a stack of 500ÅW/500ÅWSi/3500ÅIn_{1-x}Al_xN/AlN with x=0, 0.27 and 0.46 was deposited on Sapphire and RTA treated at temperatures up to 700°C. The dependence of the electrical properties of the contacts on the InAlN composition and the applied heat treatments is being investigated.

12:20-14:00

LUNCH

Friday June 19, 1998
Vendredi 19 juin 1998

Afternoon
Après-Midi

SESSION XIII - FET + Detectors

Chairperson: S. Denbaars, University of California Santa Barbara, USA

- L-XIII.1 14:00-14:30 - Invited -** **MICROWAVE ELECTRONICS DEVICE APPLICATIONS OF AlGaIn/GaN HETEROSTRUCTURES, Q. Chen, APA Optics, Blaine, MN 55449, USA**
The device performance of heterostructure field effect transistors (HFETs) has been improved tremendously through a continuous work in the areas of AlGaIn material quality, AlGaIn/GaN structural designs, Ohmic contacts, device layout, and experimenting with new substrates. By optimizing the sheet charge density-times-mobility product (μ_s), we have first improved the DC transconductance (G_m) to 120 mS/mm and channel current (I_{max}) to 350 mA/mm for 1 μ m-gate devices. We have then obtained shorter (0.25 μ m) gate HFETs exhibiting not only high DC G_m and I_{max} (142 mS/mm and 1.0 A/mm) but also excellent cutoff frequency (f_t) and maximum frequency of oscillation (f_{max}) of 37.5 GHz and 80.4 GHz, respectively. These devices have also shown high gain at 8.4 GHz with a power density reaching 1.7 W/mm.
Another thrust in the AlGaIn/GaN HFETs development hinges on the use of SiC substrates. We have achieved G_m and I_{max} as high as 222 mS/mm and 1.71 A/mm for HFETs grown on n-SiC. The HFETs on p-SiC have also exhibited G_m and I_{max} of 230 mS/mm and 1.43 A/mm. We have obtained f_t and f_{max} of 55 GHz and 56 GHz for HFETs on p-SiC.
The availability of high quality AlGaIn/GaN heterostructure has also permitted the implementation of such new device concept as MISFETs and power FETs. Our MISFETs have shown low gate leakage in \pm 6V gate bias range with G_m as high as 86 mS/mm. The results on these new development will also be discussed.
- L-XIII.2 14:30-15:00 - Invited -** **HIGH PRESSURE FABRICATION AND PROCESSING OF GAN, T. Suski, Unipress, Polish Academy of Sciences, 01-142 Warszawa, Poland**
GaN semiconductor is characterized by high melting temperature and high vapor pressure of nitrogen. These features determine the usefulness of high pressure of nitrogen during the growth of GaN single crystals. Moreover, the same properties of GaN limit the efficiency of annealing procedures required for variety of semiconductor technologies, e.g., post-implantation annealing, doping by diffusion. Maximum temperatures employed up to now in GaN annealing have not exceeded 1100°C. A desired increase of annealing temperatures causes a decomposition of GaN unless an elevated pressure of N₂ is supplied. In this work we report on the application of high pressure, high temperature procedures (temperatures up to 1600°C pressures up to 1.7 GPa) with the purpose of growing GaN crystals and annealing bulk crystals and epitaxial layers of GaN. We discuss physical properties of undoped and doped GaN bulk crystals (platelets with density of dislocations of about 10⁵-10⁶cm⁻² and available surface in the range of 100cm²). Concerning high pressure annealing, the most important results obtained in these studies consist of: i) drastic reduction of X-ray rocking curve widths and an increase of bandedge photoluminescence (PL) intensity with increasing annealing temperature (in as-grown, undoped epitaxial films), ii) a strong relationship between the improved structural quality (Zn- and Mg- implanted GaN films) and significant increase in the blue PL intensity, and iii) lack of impurity diffusion in bulk GaN crystal and impurity diffusion enhancement by high concentration of dislocations in GaN/Al_{0.2}O₃.
- L-XIII.3 15:00-15:20** **MATERIALS REQUIREMENTS FOR HIGH TEMPERATURE GaN BASED HETEROJUNCTION FETs, I. Daumiller, C. Kirchner*, M. Kamp*, K.J. Ebeling*, J. Off**, F. Scholz** and E. Kohn, Department of Electron Devices and Circuits, University of Ulm, 89069 Ulm, Germany; *Department of Optoelectronic, University of Ulm, 89069 Ulm, Germany; **4th Physical Institute, University of Stuttgart, 70550 Stuttgart, Germany**
For high power and high temperature FET device applications especially critical elements are the Schottky gate control diode and the buffer-layer. Schottky contacts on GaN show a thermally activated reverse current limiting high temperature which behavior. We have analyzed these characteristics up to 700°C. To minimize this effect a twin area model has been developed with a small area defect related diode in parallel to the large area Schottky contact. Thus the interface consists of a large area which contain the doping concentration and the barrier height of the CV-characteristics and a small, highly doped defect related diode generating the reverse leakage current.
For low leakage current at high temperature a thermally stable buffer-layer is important. A low activation energy conductivity over a wide temperature range is necessary. Here we have investigated buffer leakage up to 800°C.
As a result a n-channel GaN MESFET with an AlGaIn Schottky-layer and a normally undoped GaN-buffer layer grown by MOCVD on sapphire could be successfully operated up to a record temperature of 690°C. Upon cooling of the FET devices no degeneration of the characteristics was observed.
- L-XIII.4 15:20-15:40** **BREAKDOWN MECHANISMS IN (Al,Ga)N BASED PHOTODETECTORS, L. Ferguson, C. Tran and M. Schurman, Emcore Corporation, 394 Elizabeth Ave, Somerset NJ 08873, USA**
(Al,Ga)N based photodetectors both interdigital metal-semiconductor-metal and p-i-n photodetectors have been successfully grown and fabricated on sapphire substrates. However, at high bias voltages, avalanche breakdown appears to be present since a constant breakdown field of >105 V/cm was obtained. A negative temperature coefficient for the breakdown voltage was observed indicating that field assisted tunneling is occurring. The avalanche breakdown appears to be nucleated at non-uniform field distribution within the device and is observed as micro-plasmas. It will be shown that premature breakdown has been minimized by reducing the structural defect density in the (Al)GaN with a corresponding reduction in dark currents. Continuing reductions in defect densities will be key in producing viable avalanche devices.

SYMPOSIUM L

L-XIII.5 15:40-16:00

LOW PRESSURE MOVPE GROWN AlGa_N FOR UV PHOTODETECTOR APPLICATIONS, F. Omnes, N. Marengo, S. Haffouz, H. Lahreche, Ph. de Mierry, CNRS-CRHEA, rue Bernard Grégory, Sophia Antipolis, 06560 Valbonne, France; P. Hageman, Katholieke Universiteit Nijmegen, Fac. Der Natuurwetenschappen, Afd. EVSF III, Toernooiveld, 6625 ED Nijmegen, The Netherlands; E. Monroy, F. Calle, E. Munoz, Dpto. Ingeniera Electronica, E.T.S.I. Telecomunicacion, Ciudad Universitaria, 28040 Madrid, Spain
The LP-MOVPE growth conditions of AlGa_N epilayers on c-oriented sapphire have been optimized both on GaN and AlN nucleation layers, for aluminium compositions lying typically in the range 0-40%. Good structural, electrical and optical properties were obtained for AlGa_N alloys on (0001) oriented sapphire substrates, both for undoped and n-type doped epilayers. A typical FWHM of 650 arc-sec is measured for the (0002) X-ray double diffraction peak in the W-configuration of a 1µm-thick AlGa_N epilayer grown on a GaN nucleation layer, and a typical electron mobility of 75-90cm²/V.s is measured at T=300K on 2.1018cm⁻³ n-type doped AlGa_N epilayers. The low temperature photoluminescence (T=9K) performed on non intentionally doped AlGa_N epilayers with low Al contents (5 and 10%) concludes reproducibly to good optical properties with a sharp exciton-related peak, associated with two phonon replica and a total absence of low photon energy transitions. Optical transmission as well as absorption coefficient measurements using the photothermal deflection spectroscopy (P.D.S.) clearly show that the variation of the energy gap of AlGa_N with the aluminium concentration is linear. AlGa_N-based photoconductors and Schottky barrier photodiodes with good operating characteristics have been fabricated with these materials and will be presented.

16:00-16:30

BREAK

SESSION XIV - Growth

Chairperson: P. Gibart, CNRS-CRHEA, Sophia Antipolis, Valbonne, France

L-XIV.1 16:30-16:50

OPTICAL PROPERTIES OF CUBIC GaN GROWN ON SiC/Si SUBSTRATES, A. Philippe, C. Bru-Chevallier, M. Vernay, G. Guillot, Laboratoire de Physique de la Matière (UMR CNRS 5511), INSA, 20 av. A. Einstein, 69621 Villeurbanne Cedex, France and J. Hübner, B. Daudin, G. Feuillet, CEA Grenoble - DRFMC/ SP2M/ PSC, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France

The hexagonal phase of GaN has been extensively used for the realisation of functional blue LED's. However, technological problems such as incorporation of a high indium content and the inherent yellow luminescence are still difficult to overcome. Cubic GaN could be an attractive alternative because of its lower bandgap and absence of yellow luminescence. In this work we report on the optical properties of cubic GaN grown by MBE on SiC/Si substrates which present the advantages of low cost, low lattice mismatch and high thermal conductivity. Photoluminescence spectroscopy revealed two significant peaks. The one located around 3.26 eV corresponds to the excitonic recombination, with a FWHM as narrow as 14 meV. The second peak, at 3.16 eV, is attributed to a donor-acceptor transition. Depending on the growth conditions and SiC thickness the contribution of the hexagonal phase in the luminescence of the GaN layers can be eliminated. Our results show that the relatively low growth temperature (TG=640°C) used in MBE growth strongly reduces the amount of the hexagonal phase. The narrow FWHM of the excitonic transition confirms the good quality of the material, sufficient for the achievement of high quality optoelectronic devices.

L-XIV.2 16:50-17:10

IN SITU REAL TIME ELLIPSOMETRY MONITORING DURING GaN EPILAYERS PROCESSING, M. Losurdo, P. Capezzuto, G. Bruno, Plasma Chemistry Research Center, MITER-CNR, via Orabona, 4, 70126 Bari, Italy

The boom of blue-light emitting laser diodes has strongly increased the interest in the III-V nitrides epilayers. And, although blue LEDs and LASERS based on GaN heterostructures grown by metalorganic chemical vapor deposition (MOCVD) are being commercialized, the knowledge of the material properties and of the growth chemistry and kinetics is still incomplete. In this contribute, applications of in situ real time ellipsometry to the GaN processing by a remote plasma MOCVD technique are emphasized. Ellipsometry provides a non-destructive, non invasive and accurate measurements of layers and interfaces thicknesses and optical properties, with sub-monolayer resolution. The first issue addresses the problem of the interface between GaN epilayers and substrate: it will be shown how ellipsometry applies to control the substrate cleaning and nitridation processes in order to prepare a good quality buffer layer, and what new ellipsometry can reveal about the GaN/GaAs and GaN/sapphire interfaces. Also, the control and minimization of GaN surface damage by plasma processing is achieved by ellipsometry. The second issue concerns the real time monitoring of the chemistry and kinetics of the plasma assisted MOCVD growth of GaN epilayers. The potentiality of ellipsometry in providing information on the interfacial reactions, GaN layers stoichiometry, morphology and optical properties is highlighted. Finally, plasma oxidation of GaN epilayers will be investigated by ellipsometry to provide information on the oxide formation of the GaN compound to evaluate the possibility of GaON as passivating layers. The final aim is to set up an in situ controlled and integrated plasma technology for GaN-based materials, and including processes of substrate cleaning, nitridation, epigrowth and passivation.

L-XIV.3 17:10-17:30

LOW TEMPERATURE BUFFER GROWTH TO IMPROVE HYDRIDE VAPOR PHASE EPITAXY OF GaN, Jeong-wook Lee, Ho-sun Paek, Jae-In Lee, Ji-Beom Yoo, Sungkyunkwan University, 300 Chunchun-dong Jangan-gu, Suwon, Korea and Dong-Wha Kum, Metal Alloy Design Center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

Two step method of Hydride Vapor Phase Epitaxy(HVPE) was investigated to grow thick GaN-film on the (0001) sapphire substrate using ammonia(NH₃), chlorinated gallium(GaCl) and nitrogen carrier gas. Chlorinated Ga and NH₃ was used to grow GaN-buffer layers at 550 - 650°C, and then GaN-film was grown at 1125°C. Surface roughness after the low temperature buffer growth was measured by atomic force microscopy(AFM), and its effect on GaN-film was analyzed by double crystal x-ray diffractometer(DCXR) and electron microscopies(SEM and TEM). Direct correlation between the AFM roughness(in terms of the RMS value) of the buffer layer surface and crystalline quality of the GaN-film was observed. That is, the HVPE GaN-film exhibited the smallest FWHM value of DCXR when it was grown on the GaN-buffered condition with minimum AFM roughness. It has been also observed that a slow cooling under NH₃ flow after the HVPE growth improved the surface morphology of the GaN-film significantly. The nature of GaN-buffer layer grown by the chlorinated Ga and NH₃ and its effect on GaN-film growth will be discussed in detail.

END OF SYMPOSIUM L

SYMPOSIUM L

SYMPOSIUM L
POSTER SESSIONS

Tuesday June 16, 1998
Mardi 16 juin 1998

Afternoon
Après-Midi

Poster Session I
18:00-20:00

- L-I/P1** **TERTIARYBUTYLHYDRAZINE: A NEW PRECURSOR FOR THE MOVPE OF III NITRIDES, U.W. Pohl,** C. Möller, K. Knorr, W. Richter, J. Gottfriedsen, H. Schumann, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany; A. Fielicke, K. Rademann, Humboldt-Universität zu Berlin, Bunsenstr. 1, 10117 Berlin, Germany
The high stability of ammonia stimulates the search for alternative nitrogen precursors for the MOVPE of group III nitrides. Tertiarybutyl-ligands as a replacement of hydrogen in novel precursors are highly interesting due to a weak carbon-metal bond strength favouring a low decomposition temperature. We studied the pyrolysis of tertiarybutylhydrazine (tBuHy, (CH₃)₃C(H)NNH₂) which has a convenient stability and vapor pressure, and grew GaN epilayers using tBuHy and Me₃Ga. Quadrupole mass spectra (QMS), recorded at 0.1 mbar gas ambient and 10-6 mbar QMS sampling pressure, respectively, show that the thermal decomposition of tBuHy starts at about 200°C by homolytic cleavage into •NH₂ and tBuNH• which is detected as (CH₃)₂CNH₂ in mass spectra. Almost complete decomposition of tBuHy is observed above 350°C under QMS conditions. Mirror-like GaN epilayers were grown on GaAs(001) and Al₂O₃(00-1) substrates at 650°C and a V/III ratio of 70. On GaAs, the structural quality of GaN sensitively depends on nitridation prior to growth. Reflectance anisotropy spectra recorded in situ show that conditions which cause a Ga-terminated surface induce a rough morphology.
- L-I/P2** **PULSED LASER DEPOSITION OF GaN THIN FILMS, M. Cazzanelli, D. Cole, J.F. Donegan and J.G. Lunney,** Department of Physics, Trinity College, Dublin 2, Ireland
Thin films of wurtzite gallium nitride have been grown by pulsed laser deposition (PLD) using KrF excimer laser ablation of sintered GaN on to sapphire substrates at various temperatures in vacuum and in reactive atmospheres of nitrogen and ammonia. A time-of-flight ion probe was used to study the plasma transport through the gas, and in situ optical reflectometry was used to monitor the film thickness. The crystalline quality and surface morphology were studied using X-ray rocking curve analysis and Atomic Force Microscopy (AFM). Resistivity and Hall measurements were used to find carrier density and mobility in the range 77-300 K. The optical transmission and photoluminescence properties at room temperature (RT) were also measured. The films grown in nitrogen at 700°C were p-type and had very low carrier densities of about 7x10² cm⁻³, with RT mobilities of up to 600 cm² V⁻¹ s⁻¹. These films showed strong luminescence with a peak at 3.247 eV and a long lifetime on the order of a few ns at 300 K. The films grown in ammonia were n-type and more heavily doped.
- L-I/P3** **OPTICAL CHARACTERIZATION OF INTERFACE PROPERTIES FOR HEXAGONAL GaN GROWN BY MBE ON GaAs, S. Shokhovets, R. Goldhahn, G. Gobsch, Institut f. Physik, TU Ilmenau, PF 100565, 98684 Ilmenau, Germany, and T.S. Cheng, C.T. Foxon, Department of Physics, University of Nottingham, Nottingham NG7 2RD, UK**
Reflectivity studies in the energy range from 1.4 eV to 3.8 eV have been carried out to study the influence of MBE growth conditions on the interface properties of hexagonal GaN films on GaAs substrates. Prior to the analysis, the experimental spectra were corrected in order to exclude light scattering contribution caused by surface roughness. The remaining discrepancy between the corrected reflectivity and that one calculated for a smooth homogeneous GaN layer on GaAs is related to an interface layer between the substrate and the film with an effective refractive index different to that of both bulk GaAs and GaN. Quantitative analysis revealed a pronounced correlation between the growth conditions and parameters of the interlayer. In particular, growth on (001) substrates results in a more extended interface compared to that for (111)B orientation. Increasing growth temperature leads to a thicker interface layer and essential changes of its optical properties for films grown on (111)B substrates. This effect has been found to be reduced by nitridation of the substrate or an initiated growth at low temperatures. The properties of the interface layer will be discussed with respect to columnar growth of GaN and outdiffusion of Ga and As atoms which promotes the formation of voids in the substrate/film interface.
- L-I/P4** **CRYSTALLINE QUALITY OF GaInN/GaN HETEROSTRUCTURES, Q. Liu, G. Brockt, and H. Lakner, Gerhard-Mercator-Universität Duisburg, Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany, and F. Scholz, A. Sohmer, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany**
Group III-nitride heterostructures have attracted much attentions because of their application potential in high power, high temperature devices and light emitting devices in the visible and ultra-violet range. In this contribution wurtzite InGaN/GaN heterostructures grown by metalorganic vapor phase epitaxy were studied using cathodoluminescence (CL) combined with secondary electron microscopy (SEM), scanning transmission electron microscopy (STEM), and high resolution x-ray diffractometry (HRXRD). The surface morphology of samples containing InGaN layers is dominated by three types of defects: mesa-like hexagonal structures, hexagonal pyramids and micropipes. The luminescence efficiency as well as the emission wavelength are influenced by these defects. The detailed spatially resolved CL experiments show a blue-shift of the CL emission on defect positions, which indicates a variation of the local chemical composition of InGaN epilayers. This proposition is examined by STEM. To study the interface quality HRXRD as well as STEM was used. For InGaN/GaN single quantum wells both HRXRD and STEM results indicate the two-dimensional growth if the well width is small (e. g. smaller than 7 nm). In SL structures, panchromatic CL images show intensity inhomogeneity in a 1 µm scale, which can be related to variations of the local interface quality. STEM measurements show an increasing SL period thickness in the growth direction.

- L-I/P5** INFLUENCE OF GaN BUFFER LAYERS ON THE STRUCTURAL PROPERTIES OF MBE GROWN GaN LAYERS, V. Kirchner, R. Ebel, H. Heinke, H. Selke, S. Einfeldt, and D. Hommel, University of Bremen, Kufsteiner Str. NW1, 28359 Bremen, Germany
By high resolution X-ray diffraction a drastic influence of low-temperature buffer layers with different thicknesses on the structural properties of MBE grown GaN layers was detected. For 3 nm and 10 nm buffer layers the full width at half maximum (FWHM) of the triple-axis rocking curves of the (0002) GaN peak achieved minimum values of about 50 arcsec, which are comparable to best literature data. These curves show a characteristic shape with a very sharp peak on a broad underground. The small FWHM as well as additionally observed thickness interferences point to high structural quality, whereas high resolution TEM shows a lot of small columns parallel to the surface normal and a high density of threading dislocations. Measurements of reciprocal space maps and triple axis scans along selected directions in reciprocal space for symmetric and asymmetric reflections were made in order to clarify this discrepancy. In contrast to previous reports for MOCVD layers, no influence of the buffer layer on the strain state of the GaN layers was found.
- L-I/P6** X-RAY ANALYSIS OF THE TEXTURE OF HETEROEPITAXIAL GALLIUM NITRIDE FILMS, N. Herres, H. Obloh, K. Bachem, Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, 79108 Freiburg, Germany, and K. Helming, Institut für Metallkunde u. Metallphysik, TU Clausthal, Grosser Bruch 23, 36678 Clausthal, Germany
Gallium nitride is a most promising material for photonic and electronic applications. The preparation of gallium nitride films by deposition from the vapor phase (MOCVD, MBE) may suffer from an occurrence of multiple orientations and a mixture of the wurtzite (2H) and the sphalerite (3C) polytypes as long as the nucleation and the deposition conditions are not optimized. Thus, analytical techniques for assessing the structural quality of these films are required. We use X-ray texture diffractometry with a dedicated geometry and various scanning techniques to check for the presence of unwanted crystallographic phases and orientations in a quick and semi-quantitative manner. We analyzed a variety of GaN films showing a strong presence of the 2H and 3C polytypes, to determine the origins of polycrystalline growth. These films were deposited under non-optimal conditions by MOCVD and MBE on sapphire substrates. From X-ray polefigures and approximations of the texture by model components we found that most 2H orientations and all 3C orientations were interrelated by stacking faults on {0001} and {111} planes, respectively. If a single crystalline film orientation is wanted, a suppression of stacking faults must take place during the growth of the GaN films. This has been achieved under optimized MOCVD conditions. As evidenced by X-ray diffractometry, these films are single crystalline, phase pure 2H GaN films with small mosaicity spreads.
- L-I/P7** COAXIAL RF-MAGNETRON NITROGEN ACTIVATOR FOR GaN MBE GROWTH, V.N. Jmerik, V.V. Mamutin, V.A. Vekshin, T.V. Shubina, S.V. Ivanov, P.S. Kop'ev, A.F. Ioffe Physico-Technical Institute, 194021, St. Petersburg, Russia
The perspectives of an MBE technique for growth of GaN-based nanostructures stimulate the development of efficient nitrogen exciters. We report on the first demonstration of epitaxial growth of GaN epilayers on GaAs, Al₂O₃ and NdGaO₃ substrates by MBE equipped with a new type of the compact coaxial magnetron (CCM) nitrogen exciter based on the RF capacitively coupled discharge. Using optical emission spectroscopy, the output nitrogen flux has been controlled as a function of pressure, RF-power and magnetic field. The growth has been monitored *in situ* by RHEED. The structural study of the samples has been performed by SEM and XRD as well as by room- and low-temperature photoluminescence. Electrical properties have been characterized by C-V measurements. The growth rate as high as 500 nm/h is obtained with RF power lower than 200W and extremely low pumping rate (350 l/s) at reasonable quality of the epilayer (27 meV FWHM of near band-edge PL line at 77K on the GaAs(113) substrate). The possibilities of MBE growth of GaN cubic and hexagonal modifications have been demonstrated.
- L-I/P8** STUDY OF c-BN FILMS DEPOSITED ON DIAMOND FILMS, J. Pascallon, V. Stambouli, D. Bouchier, G. Nouet*, F. Silva**, A. Gicquel**, Institut d'Electronique Fondamentale, Bât 220, Université Paris-Sud, 91405 Orsay cedex, France, *LERMAT, ISMRA, Bd du Maréchal Juin, 14050 Caen, cedex, France, **LIMHP, université de Villetaneuse, Av. J.B. Clément, 93430 Villetaneuse, France
In an attempt to make heteroepitaxy of cubic boron nitride (c-BN) on diamond, diamond films were used as substrates for c-BN thin film deposition. The c-BN films were deposited by Ion Beam Assisted Deposition (IBAD) using a mixture of nitrogen and argon ions on diamond films. The diamond films were deposited on Si substrates by Plasma Enhanced Chemical Vapor Deposition (PECVD) and exhibited different values of surface roughness ranging from 10 to 90 nm (in R_{rms}). The microstructure of these c-BN films has been studied using *in-situ* Reflexion Electron Energy Loss Spectroscopy (REELS) analyses at different primary energy values, Fourier Transform Infra Red spectroscopy and High Resolution Transmission Microscopy (HRTEM). The fraction of cubic phase in the c-BN films was depending on the roughness of the diamond surface. Indeed, as expected, this fraction in cubic phase was optimized in the case of the smooth surface presenting no particular geometrical effect for the incoming energetic nitrogen and argon ions during the deposition. The films were nanocrystalline with columnar grains. The presence of the cubic phase was clearly confirmed in the bulk of the film while the near surface region was sp² bonded as shown by the position of the plasmon peak from the REELS analyses performed at low electron primary energy (150 eV). A study focused on the interface between the c-BN film and the diamond substrate was performed showing the commonly observed layered structure of c-BN films, i.e. a well textured c-BN volume lying on a h-BN basal layer with the (00.2) planes perpendicular to the substrate.
- L-I/P9** LP-MOCVD GROWTH OF GaN ON SILICON SUBSTRATES—COMPARISON BETWEEN AlAs AND ZnO BUFFER LAYERS, A. Strittmatter, A. Krost, V. Türc, M. Straßburg, and D. Bimberg, J. Bläsing*, T. Hempel*, and J. Christen*, Institut f. Festkörperphysik, Technische Universität Berlin, Sekr. PN 5-2, Hardenbergstr. 36, 10623 Berlin, Germany, *Institut f. Experimentelle Physik, Otto-von-Guericke Universität Magdeburg, PO Box, 10427 Magdeburg, Germany
Low-pressure MOCVD growth of GaN layers on sputtered ZnO/Si(111) and epitaxial grown AlAs/Si(111) has been studied. From X-ray diffraction monocrystalline, and hexagonal GaN layers on top of the epitaxial AlAs buffer layers were confirmed. The spectra of the GaN/ZnO/Si(111) samples show a polycrystalline structure caused by the ZnO buffer layer. No differences between Si(111) and Si(001) substrates were found for all measurements for the GaN/ZnO/Si samples. The impurity incorporation into the GaN layers was investigated by SIMS. Si doping in all layers is below the detection limit. For samples with a ZnO buffer layer, we observed Zn and O enrichment near the GaN/ZnO interface. Luminescence spectra were obtained by cathodoluminescence measurements. For ZnO buffer layers, the spectrum is dominated by excitonic recombination at about 3.47 eV. In contrast, the spectrum of a GaN/AlAs/Si sample shows besides the excitonic peak a broad luminescence band around 2.9 eV.

- L-I/P10** **IMPACT OF THE ZnO BUFFER LAYER ON THE MORPHOLOGY AND THE OPTICAL PROPERTIES OF GaN**, J. Christen, A. Hoffmann*, Institut f. Exp. Physik, Otto-von-Guericke-Universität Magdeburg, Germany, *Institut f. Festkörperforschung, Technische Universität Berlin, Germany
We report on highly spatially resolved luminescence experiments in GaN and their correlation with the morphology obtained from SEM and AFM. Cathodoluminescence (CL) microscopy directly visualizes the strongly inhomogeneous, columnar structure of the GaN layer. Locally well separated morphological channels are clearly visible. Two different categories of these parallel channel can be separated: One type of channels (blue channel) emits near band gap GaN luminescence. In addition strongly localized "red channels", elongated along the c-direction (embedded in between these "blue channels") are clearly resolved by CL microscopy. The nature of both luminescence and morphology channels is discussed in terms of dissociation of ZnO and consecutive incorporation of O as the dominating donor into the growing GaN epilayer as well as the diffusion and accumulation of Zn-acceptors along the dislocation channels running like "pipes" in c-direction from the interface to the GaN surface.
- L-I/P11** **THE INFLUENCE OF MOCVD PROCESS SCHEME TO THE OPTICAL PROPERTIES OF GAN LAYERS** M. Ciorga, L. Bryja, J. Misiewicz, R. Paszkiewicz, R. Korbutowicz, M. Panek, B. Paszkiewicz, M. Tlaczala, Wrocław University of Technology, Institute of Physics, Wyspińskiego 27, 50-370 Wrocław, Poland
The GaN layers were grown on sapphire substrates using atmospheric pressure MOVPE system. New, complicated process scheme was developed to improve the epitaxial layers quality. Additional buffer layers, grown with increasing temperature and increasing V/III ratio, were inserted between low temperature buffer layer and high temperature GaN overlayer grown on it. This multi-buffer layer strategy allowed us to obtain GaN epitaxial layers with properties superior to those grown in conventional process scheme. The photoluminescence study both in liquid nitrogen and room temperatures were performed. The blue exciton line as well as the yellow one were observed. The correlation between GaN layers photoluminescence and epitaxial process parameters were established and compared to their electrical and structural characteristic.
- L-I/P12** **CHARACTERISTICS OF UNDOPED AND MAGNESIUM DOPED GAN FILMS GROWN BY LASER INDUCED MBE**, M. Gross, G. Henn, J. Ziegler, M. Klose, N. Wieser and H. Schröder, DLR Stuttgart, Institute of Technical Physics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany
Epitaxial GaN films were grown on Sapphire (0001) and 6H-SiC (0001) by laser ablation of a Ga target in a molecular nitrogen atmosphere. We used a Nd:YAG laser with 30 ps pulses and a pulse rate of 1-2 kHz.
The film growth was studied as a function of substrate temperature, laser pulse energy and N₂ flow. The films showed good crystalline properties. X-ray rocking curve measurements revealed a FWHM of 12 arcmin for films on sapphire and 9 arcmin for films on 6H-SiC. The rms roughness of the film surfaces, investigated by AFM was found to be 2 nm.
Investigations on the undoped films revealed a Hall background carrier concentration of $6 \times 10^{17} \text{ cm}^{-3}$ and an excitonic near band edge emission at 3.47 eV in the low temperature PL spectrum.
PL spectroscopy and SIMS measurements showed that Mg incorporation in the GaN films was achieved by simultaneous laser ablation of a Mg target during the growth process. The Mg content was varied by different ablation times. Mg incorporation effectiveness of the growth process and electrical activity of the doping species was studied.
- L-I/P13** **WITHDRAWN**
- L-I/P14** **GALLIUM METAL INCLUSIONS IN GAN**, A.V. Blant, T.S. Cheng, D. Korakakis, I. Harrison, L. Flannery, R. Campion, Department of Physics, University of Nottingham, University Park, Nottingham NG2 7RD, UK and S.V. Novikov, Ioffe Physical-Technical Institute, St.Petersburg 194021, Russia
The Group III-Nitrides are currently being used extensively for visiblelight emitting diodes(LEDs) and FETs and will form the basis of blue/UV laser diodes (LDs). At present LEDs have acceptable lifetimes, but LDs suffer from rapid degradation in part due to contact migration down nanopipes or sub-grain boundaries. We have been investigating this phenomenon and have discovered one possible related mechanism, gallium metal inclusions in GaN grown by MBE under certain conditions. We have studied a variety of GaN epitaxial layers grown on various different substrates including GaAs, Si, sapphire and HVPE GaN grown on SiC. In our initial investigations mechanical abrasion induced during device processing revealed metallic-looking features on the surface in high-magnification optical studies. To confirm this idea we etched such surfaces in HCl and all trace of the metallic features disappeared, which reappeared upon further mechanical abrasion of the surface. XPS studies of the as grown material showed a single peak for the Ga 2p_{3/2} bound to nitrogen, but after abrasion a doublet is observed. The new peak has now been shown to be due to oxidised Ga on the surface. We will discuss the origin and avoidance of such Ga metal inclusions.
- L-I/P15** **MODELLING OF THE DEFECT STRUCTURE IN GAN MOCVD THIN FILMS BY X-RAY DIFFRACTION**, F. Huét, M-A. di Forte-Poisson, Thomson-CSF/LCR, Orsay, France; J. di Persio, Université de Lille, Villeneuve d'Ascq, France; B.Pécz, Res. Inst. for Tech. Phys., Budapest, Hungary
Due to large lattice and thermal mismatches between GaN and sapphire substrates (respectively 16% and 80%), lots of dislocations originate during the epitaxial growth of the layers. TEM investigations of hexagonal GaN films grown by MOCVD have shown dislocations densities in the range of 10^{10} cm^{-2} . These dislocations are shown to be threading from the GaN/sapphire interface normal to the sample surface, and often array in walls which form boundaries between small crystal subgrains.
We have applied the Hordon-Averbach's model to the determination of grain size and dislocation densities in GaN layers using X-ray diffraction. The model evaluates the separate contribution of lattice tilting, strain and particle size to the broadening of the experimental full width at half maximum (FWHM) of some Bragg's reflexion peaks. We show that a clear picture of tire dislocation distribution and tilts within the GaN structure can be obtained using this model. From a careful comparison of measurements carried out on symmetrical or asymmetrical reflexions, we confirm that the quite low value obtained for the (0002) reflexion (in the order of 30 arcsec for our samples) is a good indication of the very high quality of the material. These results are supported by TEM investigations. Full details will be given at the conference.
- L-I/P16** **ANALYSIS OF COMPOSITION FLUCTUATIONS IN ALGAN**, B. Neubauer, D. Gerthsen, Laboratorium für Elektronenmikroskopie, Universität Karlsruhe, 76128 Karlsruhe, Germany and O. Ambacher, M. Stutzmann, Walter Schottky Institut, Am Coulombwall, TU München, 85748 Garching, Germany
An Al_{0.25}Ga_{0.75}N/GaN transistor structure on an Al₂O₃(0001) substrate and Al_xGa_{1-x}N layers with different Al contents on a 6H-SiC(0001) substrate were studied by high-resolution transmission electron microscopy. The Al content of the layers on SiC varied nominally from 0% to 100%.
Analysing the local lattice parameters on an atomic scale allows the detection of composition fluctuations on the basis of Vegard's law. By the digital analysis of lattice images (DALI) the intensity maxima positions are detected in HRTEM cross-section images which can be considered as a fingerprint of the local lattice parameters if the thickness of the specimen does not significantly change and imaging conditions without chemical shifts are chosen. The lattice parameters of the ternary compounds are measured with respect to a reference lattice which is defined in a large area to yield the average lattice constant of the layer and which is superimposed on the whole investigated area.
Different areas in the Al_{0.25}Ga_{0.75}N layer of the transistor structure were investigated which either show homogeneous or "striped" contrast. The "striped" areas show a strong periodic decomposition with a period of 1nm consisting of 1 monolayer of AlN and about 3 monolayers of GaN. These results could be confirmed by the diffractogram showing superlattice reflections.
The other regions do not show significant composition fluctuations.

- L-I/P17** EPITAXY OF GALLIUM NITRIDE BY HYDRIDE VPE, Q. Parillaud, V. Wagner, H.J. Bohlmann, and M. Ilegems, Institute of Micro- and Optoelectronics, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland
We report ongoing experiments on the growth of thick GaN epitaxial layers by Hydride VPE, using a large scale horizontal Aixtron reactor. Growth rates of 50µm/h were achieved on 5 cm diameter substrates under standard flow conditions (N₂ = 3.6 l/min carrier gas, NH₃ = 1.2 l/min and HCl = 12 ml/min over liquid gallium). Results on (0001) sapphire substrates, on substrates covered with a 2 µm high temperature MOVPE GaN layer and on substrates covered with only a 20 nm low temperature MOVPE buffer layer, show that consistently smoother morphologies are achieved on the substrates covered with high or low temperature GaN starting layers. The layer crystallinity as monitored by X-ray diffraction was comparable (< 600 arcsec FWHM comparable to the starting layer) in all cases. The results of this preliminary study will be used as a starting point for the optimization of the experimental conditions for the epitaxial lateral overgrowth on patterned GaN films on sapphire.
- L-I/P18** DEPOSITION AND STRUCTURAL INVESTIGATION OF HEXAGONAL-CUBIC BORON NITRIDE FILMS, A. Bonizzi, C.E. Bottani, R. Checchetto*, A. Miotello*, P.M. Ossi, INFN-Dipartimento di Ingegneria Nucleare, Politecnico di Milano, via Ponzio 34/3, 20133 Milano, Italy; *Dipartimento di Fisica, Università di Trento, 38050 Povo (TN), Italy
Besides being hard and corrosion resistant, cubic BN is attractive as electrically insulating material, as heat sink for electronic devices, and as light emitting p-n junction. BN potentiality as a device material is limited by the constraint to deposit at low temperature films with a large fraction of cubic phase, yet avoiding stability problems resulting from the high compressive stresses required to nucleate it. BN films of thickness in the hundreds of nanometers range were prepared near room temperature by RF sputtering, with different RF bias values, and argon-nitrogen atmospheres of various composition. The films were deposited on substrates including Si (100), copper and stainless steel. Film composition was tested by Auger electron spectroscopy and the structure was studied by FTIR and micro-Raman spectroscopies: the films are highly disordered, and contain a relevant fraction of tetrahedral coordination, besides graphitic bonds. Spectroscopy results were compared with hardness data obtained by nanoindentation.
- L-I/P19** GaN EPILAYERS ON TILTED SUBSTRATES, C. Trager-Cowan, P.G. Middleton, K.P. O'Donnell, University of Strathclyde, Scotland and S.D. Hersee, Center for High Technology Materials, University of New Mexico, Albuquerque NM, USA
Growth of GaN on tilted sapphire substrates is expected to relieve certain problems associated with lattice mismatch. Three silicon-doped 3µm thick GaN samples were grown simultaneously by metalorganic chemical vapour deposition on (0001) sapphire substrates misoriented by 0°, 4° and 10°. We report here a comparative study of these samples by photoluminescence (PL) spectroscopy, atomic force microscopy (AFM) scanning electron microscopy (SEM) and cathodoluminescence (CL) imaging. PL of the 0° and 4° samples shows bound exciton (BE) emission near 3.475 eV and a low level of yellow band emission. The peak intensities of both emission bands are a factor of 2 higher for the 4° sample. In the 10° sample, the BE band is 3x stronger than in the 0° sample but there is no discernible yellow band. However, a number of additional bands appear at 3.41 eV, 3.31 eV and 3.28 eV, which we attribute to structural defects, cubic inclusions and DA pair recombination respectively. The appearance of these bands point to an abrupt degradation of the structural quality of the 10° sample compared to the others. This degradation is confirmed by AFM studies. On a 20 µm x 20 µm image the 0° and 4° samples exhibit smooth surface morphologies while the 10° sample shows a high density of hexagonal pits. Finally, SEM images reveal the surface of the 10° sample to be "streaked" and pitted. CL images at 3.48 eV (bound exciton region) show random spotty emission, while those at 3.28 eV and 3.41 eV exhibit a streaky appearance similar to the SEM image, suggesting that these luminescence bands are associated with structural defects.
- L-I/P20** MO-MBE GROWTH OF GaN ON 6H-SiC WITHOUT BUFFER LAYER, T. Honda, Y. Yamamoto and H. Kawanishi, Dept. of Electron. Eng., Kohgakuin University, 2665-1 Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan
GaN layers have been grown directly on (0001) 6H-SiC using metalorganic molecular beam epitaxy (MO-MBE). The direct growth of GaN is important to realize a UV laser with a substrate-side contact, because a high Al composition area was created in an AlGaIn/6H-SiC interface during the AlGaIn direct growth. A thermally heated ammonia and a triethylgallium were used as sources for the GaN growth. Streak lines were observed in RHEED patterns of GaN layers. Those indicate that the two-dimensional growth of GaN have been succeeded without a buffer such as AlN.
- L-I/P21** SIMS ANALYSIS OF Mg DOPED GaN FILMS PREPARED BY HWE, A. Ishida, K. Matsuda, S. Chu, F. Tanoue*, S. Sakakibara*, K. Ishino, S. Fuke and H. Fujiyasu, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8561, Japan, *YAMAHA Corp., 203 Matsunokijima, Toyo-oka 438-0192, Iwata-gun, Japan
Mg doped GaN films were prepared by hot wall epitaxy, and Mg and oxygen concentrations were measured by secondary ion mass spectrometry (SIMS). Two kinds of doping methods were performed: The one was modulation doping of Mg and another was continuous doping. The modulation doping was performed by Flip-Flop method in which growth was interrupted on the hot wall of Mg₃N₂ impurity after every 150Å thick growth of GaN, and the continuous growth was performed by introducing Mg impurity into the GaN hot wall. SIMS analysis of modulation doped GaN films showed clear periodic Mg distribution even though the growth temperature is as high as 1000°C. Background oxygen concentration of modulation doped GaN films were of order of 10¹⁸cm⁻³, and that of continuous growth was one order of magnitude lower than that of modulation doping. The oxygen concentration increased with the increase of Mg impurity concentration both for modulation doping and continuous doping. The oxygen concentration for continuous growth was restricted to one order of magnitude lower than that of the Mg impurity concentration.
- L-I/P22** INFLUENCE OF THE ASSISTING ION BEAM ENERGY RANGES ON THE BN FILMS STRUCTURE, I.V. Svačkovski, D.A. Golosov, A.P. Dostanko, D.A. Kotov, S.M. Zavadski, Belarussian State University of Informatics and Radioelectronics, Brovka Street 6, 220027 Minsk, Belarus
Ion assisted deposition is one of preferable methods of formation BN films with large contents of a cubic phase. Together with other process parameters the choice of a bombardment ions energy range has important significance on primary growth of a certain phase BN thin films. The purpose of this work was investigation the influence of various assisting ion energy ranges on primary formation of a phase BN films, received by a dual ion beam deposition technique. As source of ions assisting beam was used the original double closed-drift ion source, capable to generate ions with energy from 25 up to 1100eV at ion beam current up to 1A. Current density of bombardment ions (Ar⁺/N₂⁺) was changed within the limits of 50-400µA/cm². The h-BN target was sputtered by Ar⁺ ions. The substrates temperatures was 50-700°C. The compositions and structure of the deposited films were investigated by IR spectroscopy and transmission electron microscopy methods. Dependence between the deposition condition (ion/atom and Ar/N₂ ratios, substrates temperature) for different energy ranges of bombardment ions and phase parameters films was determined.
- L-I/P23** WITHDRAWN

- L-I/P24** TEM STUDY OF {1010} INVERSION DOMAINS IN GaN GROWN ON (0001) SAPPHIRE SUBSTRATE, V. Potin, P. Ruterana and G. Nouet, LERMAT, UPRESA 6004, ISMRA, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France

Recent technological breakthrough has demonstrated the possibility to fabricate blue laser diodes based on GaN. However, it is also recognized that the layers used still contain large densities of defects. During the growth of a GaN layer over sapphire, very small domains can be formed crossing the whole layer. Their width is of few nanometers and they are limited by {1010} facets. A conventional TEM analysis in the Bright Field and Dark Field modes along the [1010] zone axis shows clearly that they have an inversion character. The atomic structure of their interface with the matrix was analysed by high resolution electron microscopy and a pure inversion model without translation was found to agree with the experimental images.

At present, CBED experiments are carried out to determine the polarity of the matrix and consequently of the domains. Moreover, a TEM analysis of the fringes observed in two-beam conditions is carried out as well.

- L-I/P25** DISORDERING PROCESSES IN ALUMINIUM NITRIDE, A.P. Garshin, St. Petersburg State Technical University, Polytechnicheskaya 29, 195251 St. Petersburg, Russia and V. Shvaiko-Shvaikovskiy, Institute of Silicate Chemistry, Russian Academy of Sciences, ul. Odoevskogo 24/2, 199155 St. Petersburg, Russia

The processes of defect formation (including Schottky, Frenkel, and anti-Frenkel mechanisms) in aluminium nitride are analyzed within the quasi-chemical approximation. The solution of the equations describing disordering under various conditions of electrical neutrality yielded the dependences of defect concentration on partial nitrogen pressure under equilibrium conditions. Experimental proof was found of the theoretical analysis results of point defects formation by Frenkel mechanism in AlN.

- L-I/P26** ARSENIC ON CUBIC GaN SURFACES: SURFACTANT EFFECT VS INCORPORATION, G. Feuillet*, H. Hamaguchi, H. Okumura, S. Yoshida, Electrotechnical Laboratory 1-1-3 Umezono, Tsukuba, Ibaraki, 305 Japan, *CEA-Grenoble DRFMC, 17 rue des martyrs, 38041 Grenoble cedex 09, France

It will be shown that the presence of Arsenic during the MBE growth of cubic GaN changes the structure of the growing surfaces and influences the structural and optical properties of the cubic epilayers. When growth is carried out on (001) cubic SiC substrates, surface reconstructions of the type 4×1 or 1×1 are observed, depending on the surface stoichiometry during growth. These surfaces become respectively 2×2 or $c(2\times 2)$ reconstructed when exposed to an arsenic flux, just like in the case where (001) GaAs substrates are used. The transition between these surface reconstructions has been followed as a function of the As flux and it could be demonstrated that above a certain critical As flux, As is incorporated in the lattice, whereas below this value Arsenic remains on the surface, smoothes the surface and is exchanged with Nitrogen atoms, thus acting as a surfactant for cubic growth. This critical As flux value depends on the growth temperature. A comparison has been carried out of the structural and optical properties of cubic GaN layers grown with or without Arsenic present during growth and for different Arsenic fluxes. It was unambiguously demonstrated that better layers are obtained when Arsenic is present, if growth is carried out at high enough temperatures. At lower temperatures, the incorporation of Arsenic in the GaN lattice degrades the quality of the cubic GaN layers.

- L-I/P27** INVESTIGATION OF THE ATOMIC STRUCTURE OF THE PURE EDGE AND A + C THREADING DISLOCATIONS IN GAN LAYERS GROWN BY MBE, P. Ruterana, G. Nouet, V. Potin, R. Bonnet*, M. Loubradou*, Laboratoire d'Etudes et de Recherches sur les Matériaux, UPRESA CNRS 6004, Institut Sciences de la Matière et du Rayonnement, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France; *Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, URA CNRS 29, Institut National Polytechnique de Grenoble, Domaine Universitaire, B.P. 75, 38402 Saint-Martin-D'Hères Cedex, France

GaN layers for optoelectronic applications are epitaxially grown on sapphire, which exhibit a misfit of 16%. This results in the formation of layers containing high densities of defects ($10^9 - 10^{10} \text{ cm}^{-2}$) which are mainly : a, a + c and c threading dislocations which originate at the interface and propagate through the active GaN layers. The layers results in a mosaic structure of subgrains limited by these dislocations. The obtained layers are used to fabricate very efficient optoelectronic devices such as LED's and laser diodes, which implies that these defects do not have a high electrical activity. In this work, we present the first results obtained on the atomic structure of the a and a + c dislocations which has a mixed character. The techniques used are HREM and extensive image simulation. The models are obtained by anisotropic elasticity, and used in image simulation by the electron microscopy software, they are eventually compared to the experimental micrographs.

- L-I/P28** CHEMICAL BEAM EPITAXY OF GaN ON SAPPHIRE, M. Kappers, J.-L. Guyaux, J. Olivier, R. Bisaro, C. Gratepaign and J.-C. Garcia, Thomson-CSF LCR, Domaine de Corbeville, 91404 Orsay Cedex, France

Gallium nitride films were grown on (0001) sapphire substrates by Chemical Beam Epitaxy (CBE) using triethylgallium (TEGa) and ammonia (NH₃) precursors. Prior to the GaN epilayer growth at 850°C, a thin crystalline GaN nucleation layer was deposited at 550°C. Surface morphology, structural, and optical properties of the 1 µm thick epitaxial layers were investigated versus the thickness of the nucleation layer (NL). Atomic force microscopy images show that the epilayer is composed of ordered hexagonal islands (up to 10 µm in diameter) which have an rms roughness as low as 1.4 nm measured over $3\times 3 \mu\text{m}^2$. The films become more rough with decreasing NL thickness, due to a decreasing island size. High resolution X-ray diffraction results indicate that the epitaxial layers are of similar structural quality (rocking curve FWHM of 1200 arc sec). The level of unintentional carbon doping is high in all films, with a minimum value of $4\times 10^{19} \text{ cm}^{-3}$ for the epilayer grown on a 30 nm thick nucleation layer. In the photoluminescence spectra at 10 K, the GaN samples display a band edge signal at 3.47 eV, accompanied by a broad yellow luminescence at 2 eV. The FWHM of the band edge signal is the smallest for the sample with a 30 nm thick NL, i.e. 52 meV. These early results indicate that the CBE technology using TEGa and NH₃ precursors is a promising candidate for the growth of high quality nitride films. In our paper, we will discuss the progress in achieving this goal.

- L-I/P29** HIGHLY TEXTURED HEXAGONAL AlN FILMS DEPOSITED AT LOW TEMPERATURE BY REACTIVE CATHODIC SPUTTERING, F. Brunet, F. Randriamora, A. Deneuville, P. Germi and M. Pernet, Lb. Cristallographie and LEPES, CNRS, BP 166, 38042 Grenoble Cedex 9, France

AlN thin films can be used for a large number of applications (piezoelectric properties, cold cathode, ...) where the existence and the control of a texture is important. For most of them the large area and deposition at low temperature on glass are required.

We study here the influence of the Si(111), Si(100) and silica substrates, of the N₂ content (53 and 72%) and of the substrate temperature (RT to 700°C) on the texture of about 500 nm thick AlN films formed by magnetron reactive cathodic sputtering.

All films exhibit two directions of texture, in the directions (002) and (101), whose relative amounts depends on the conditions of preparation. The best textures are obtained in the (002) direction at low temperature 300°C with the 72% N₂ reactive mixture independently of the nature of the substrate, therefore even on the amorphous silica substrate. They are quite excellent (MRD 2 around 20). Good (101) textures (MRD 2 around 8) are obtained at 250°C with the 53% N₂ reactive mixture with a small influence of the nature of the substrate, also even on the amorphous silica.

These results are discussed in the framework of preferential orientation of the dense (002) plans on the substrate surface from N ion bombardment of the film during its growth, while the (101) orientation would originate from a higher growth rate in this cristallographic direction. The two models will be tested by varying the total pressure and the thicknesses of the films.

SYMPOSIUM L

L-I/P30

OBSERVATION OF SILICON NANOCRYSTALS IN SiN_x FILMS FORMED BY EXCIMER LASER OR THERMAL ANNEALING. M.D. Efremov, V.A. Volodin, V.A. Gritsenko, S.A. Kochubei, Institute of Semiconductor Physics SB RAS, pr. Lavrentjeva 13, Novosibirsk 630090, Russia
Silicon nitride films deposited by LPCVD on (001) Si substrates from SiH_2Cl_2 and NH_3 mixture at 760°C with $\text{SiH}_2\text{Cl}_2/\text{NH}_3$ ratios 0.5, 1.3 and 1.6 were studied using Raman spectroscopy. Because the studied films were semitransparent for wavelength of exciting light (488nm), polarization geometry of scattering was Z(XX)-Z to eliminate very intensive peak caused by scattering on Brillouin zone-center LO phonons of Si (001) substrate. Peaks appearing due to Raman scattering on Si-Si, Si-N bond vibrations in silicon nanoclusters was detected in as-deposited films. Strong changes in Raman spectra of SiN_x films appear after thermal and laser annealing, that can be interpreted as formation of silicon nanocrystals inside of the films. Thermal annealing leads to gathering of Si atoms in nanocrystals with size about 3-5nm. Using pulse excimer laser treatment (5ns) prevents diffusion of Si atoms and allows to crystallize Si nanoclusters existed in as-deposited SiN_x films. Estimated from Raman data sizes of nanocrystals were from 1.5 up to 2.5 nm depending on energy density of laser irradiation and value of excess of silicon atoms. This work was supported by Russian Fund of Basic Research.

L-I/P31

THE GROWTH OF THICK GaN ON Si SUBSTRATE USING VERTICAL HYDRIDE VAPOR PHASE EPITAXY WITH GaCl_3 . Ho-Sun Paek, Jae-In Lee, Jae-O Kwak, Su-Jeong Suh, Ji-Beom Yoo, Sungkyunkwan University, 300 Chunchun-dong Jangan-gu, Suwon, Korea

We have investigated the growth characteristics of thick GaN on Si substrate with buffer layer. The vertical hydride vapor phase epitaxy system with GaCl_3 precursor was used for the growth of GaN. AlN buffer layer was deposited on Si substrate with RF sputtering to reduce the lattice mismatch and the thermal expansion coefficient between Si and GaN. Si(100) and Si(111) were used in order to study the effect of substrate orientation on thick GaN growth. Effects of deposition parameters such as temperature, RF power and deposition time on surface roughness were analyzed using Atomic Force Microscopy (AFM) and optimized. AlN buffer layer in the range of $350\text{\AA} \sim 400\text{\AA}$ was deposited and RMS roughness was measured 0.79 \AA . We studied the effects of growth temperature, ratio and geometry of reactor on the growth of thick GaN. Surface morphology, growth rate crystallinity and optical characteristics of thick GaN were measured using AFM, Scanning Electron Microscopy (SEM), Double Crystal X-Ray Diffractometer (DCXRD) and photoluminescence.

Wednesday June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-Midi

Poster Session II

18:10-19:30

- L-II/P1** CURRENT-VOLTAGE CHARACTERISTICS OF LED BASED ON GaN EPITAXIAL FILMS, S.V. Svechnikov, P.Ph. Oleksenko, G.A. Sukach, P.S. Smertenko, S.I. Vlaskina, A.B. Bogoslovskaya, I.O. Spichak, ISP NASU, prospect Nauki 45, 252028 Kyiv, Ukraine; Nan-Ihn Cho, Sun Moon University, Churan, South Korea
The forward and reverse current-voltage characteristics (CVC) of LED on GaN epitaxial films have been investigated by differential spectroscopy. This method is based on the determination of differential slope of the curve in log-log scale in the form: $a=d \lg I/d \lg V$ and $g=d \lg a/d \lg V$. Such treatment allows to determine the fine structure of CVC.
The main peculiarity of reverse CVC is the absence of rectification. The current approximations are I~V³ and I~V⁴ in low and high bias regions, respectively. This corresponds to high injection level of both types of current carriers and to superhigh one, respectively.
The behaviour of forward CVC shows the exponent with nonideality factor $m=eV/kT$ from 6 to 8 in the bias region up to 1.5 V. Then the $a(V)$ dependence has two maxima which correspond to change of charge flow mechanism from carrier diffusion to field mechanism in the first case and to recombination barrier overcome in the second case. Just after second maximum the light emission occurs.
The CVC behaviour in temperature range from 150 K to 400 K has been discussed.
The comparison between CVC and spectral, kinetic, lux-ampere characteristics have been made in the same temperature range.
- L-II/P2** ANNEALING BEHAVIOUR AND LATTICE SITE LOCATION OF Hf IMPLANTED GaN, E. Alves, M.F da Silva, J.G. Marques*, J.C. Soares*, K. Freitag**, Instituto Tecnológico e Nuclear (ITN), EN 10, Sacavém, Portugal, *Centro de Física Nuclear da Univ. de Lisboa, Av. Prof. Gama Pinto 2, 1699 Lisboa, Portugal; **ISKP, Univ. Bonn, Nussallee Str, 53115 Bonn, Germany
The defect recovery and lattice site location of Hf implanted into GaN single crystalline epilayers were studied combining RBS/channeling and Hyperfine Interactions measurements. The RBS/Channeling measurements performed after implantation of 5×10^{14} Hf/cm² at 100 keV show that nearly all the implanted ions were incorporated into substitutional sites of the GaN lattice. The damage produced by the implantation recovers almost completely after one hour annealing at 900°C and all the Hf ions then occupy substitutional sites. The hyperfine interaction measurements were performed with the ¹⁸¹Hf/¹⁸¹Ta probe, after implantation of ¹⁸¹Hf to a fluence of 1×10^{13} Hf/cm² with 80 keV. These measurements show that the defect recovery starts already after annealing at 500°C and is complete after annealing at 900°C.
- L-II/P3** STRUCTURAL CHARACTERISATION OF Mg ION-IMPLANTED GaN, A. Wenzel, C. Liu and B. Rauschenbach, Universität Augsburg, Institut für Physik, Memminger Str. 6, 86135 Augsburg, Germany
Ion implantation is the main process for local doping of semiconductors. The main attention has to be turned to the damage build-up associated with the implantation process. It should be kept as small as possible during implantation and reduced afterwards by an appropriate annealing step. Mg-ions have been implanted at an energy of 90 keV, doses between 1×10^{14} and 5×10^{15} /cm², temperatures of 30 - 600°C and ion current densities of 0.5 - 20 μ A/cm² into 0.6 - 2.0 μ m thick GaN-layers grown on sapphire substrates by MBE to achieve p-doped material. Annealing has been executed in an RTA furnace for 15 s at 1150°C in flowing N₂. The structure has been characterised by X-Ray-Diffraction and Rutherford Backscattering/Channeling. The damage formation is studied in dependence on ion dose, current density and temperature. By annealing these damages can partially be removed. These results are compared to those of other implanted ions (C, Ca, Ar) and to the reduction of the carrier density examined by Hall- and Raman-measurements. Photoluminescence shows the formation of donor-acceptor-pairs.
- L-II/P4** RAMAN SCATTERING SPECTROSCOPIC STUDY OF CUBIC GaN AND AlN GROWN BY MBE ON SiC(3C)/Si(100), E. Bustarret, G. Bentoumi, A. Deneuve, CNRS-LEPES, BP166X, 38042 Grenoble 9, France; F. Brunet, CNRS-Laboratoire de Cristallographie, BP166X, 38042 Grenoble 9, France and J. Hübner, G. Feuillet, B. Daudin, CEA-Grenoble DRFMC/SP2M, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France
The structural properties of Zinc-blende Nitrides grown by rf-Plasma Molecular Beam Epitaxy at relatively low temperatures on cubic SiC layers deposited on (100) c-Si substrates have been investigated by X-ray diffraction and Raman scattering. Quantitative analysis showed that in some scattering geometries Raman Spectroscopy was able to detect volume fractions of the undesirable wurtzite phase as low as 10^{-3} , and that this volume fraction decreased when the surface morphology of the SiC layer was improved. Moreover, the use of confocal micro-Raman backscattering enabled us to confirm that the hexagonal to cubic ratio increased going from the nitride/SiC interface to the free surface. On the other hand, lower growth rates were found to minimize the amount of local hexagonal bonding configurations. Both in GaN and in AlN layers, the hexagonal to cubic volume ratio was shown to depend systematically on the III/V ratio, with higher wurtzite contents under nitrogen-rich conditions. These experimental results and in particular the correlation between growth conditions and the structural quality of the epitaxy are discussed in view of the various processes (including stacking-fault formation) occurring at the surface of the epitaxial layer during growth.
- L-II/P5** CARRIER TRANSPORT IN GaN GROWN BY MBE WITH DIFFERENT PLASMA SOURCES, M. Fehrer, S. Einfeldt, U. Birkle, and D. Hommel, Institute of Solid State Physics, University of Bremen, Kufsteiner Str. NW1, 28359 Bremen, Germany
GaN layers grown by molecular beam epitaxy using an electron cyclotron resonance (ECR) and a radio frequency (rf) plasma source were investigated by temperature dependent Hall effect measurements. For the ECR grown samples the carrier concentration as well as the Hall mobility changes exponentially with temperature. This phenomenon can be explained by assuming potential barriers due to electrons trapped in deep states which have to be overcome for carrier transport. A significant maximum in the extracted barrier heights and a minimum in the room temperature mobilities as a function of carrier concentration confirms this picture. A mathematical description to extract material parameters will be presented. In contrast the rf grown samples exhibit a complete different behaviour. The carriers do not completely freeze out at low temperatures but their concentration shows a minimum versus temperature. A multilayer model with an assumed highly degenerate interface layer is used to explain the experimental results of samples with different thicknesses.
- L-II/P6** ERD-MEASUREMENTS ON GROUP-III-NITRIDES, S. Karsch, A. Bergmaier, G. Dollinger, Ch. Frey and O. Schmelmer, TU München, James-Frank-Strasse, 84748 Garching, Germany; O. Ambacher, M. Stutzmann, Walter-Schottky-Institut, TU München, Am Coulombwall, 85748 Garching, Germany
Using ERD-analysis as a quantitative method to measure depth resolved elemental profiles in group-III-nitride films, the stoichiometry of Al_xGa_{1-x}N mixtures was determined. By comparing these results with x-ray diffraction data the validity of Vegard's law in the system AlN-GaN could be confirmed with high accuracy. In addition, quantitative depth profiles of impurity concentrations in group-III-nitrides can be obtained. Data of oxygen and hydrogen contaminations in magnesium doped GaN films before and after annealing will be presented.

- L-II/P7** SMOOTH GaN SURFACES BY PHOTOINDUCED ELECTROCHEMICAL ETCHING, T. Rotter, J. Aderhold, D. Mistele, O. Semchinova, J. Stemmer, D. Uffmann and J. Graul, Laboratory for Information Technology, University of Hanover, Germany
Patterning of the wide band gap semiconductors GaN and its ternary alloys AlGaIn and InGaIn is usually performed with dry etching techniques. The reason for this is the low chemical reactivity of the mentioned nitrides. Wet etching is unusual, and the defect densities cause non-uniform etch patterns. Therefore, the results are up to now not competitive to the sophisticated dry etching methods. We will report on a wet etching technique of epitaxially grown high quality GaN at room temperature resulting in high etch rates (up to 200nm/min) and smooth surfaces. Etching is done in an electrochemical cell using He-Cd laser illumination to generate electron-hole pairs responsible for the dissolution of the GaN electrode (anode). As electrolyte we commonly use a KOH based aqueous solution. The etch process is monitored via the photoinduced current (Faraday's law) and can be controlled in situ by an external voltage. The GaN etch spots are examined by mechanical profilometry and SEM. They appear to the eye mirrorlike, and the roughness is on the order of several nanometers - comparable to the unetched surfaces. The high anisotropy of this process makes it a powerful tool for structuring epilayers. Probably a part of the current is strongly related to the high material defect density. As an extension of our recent work we will present process conditions for reproducible etch depths in terms of current densities and etchant composition depending on materials properties.
- L-II/P8** LUMINESCENT PROPERTIES OF GaN THIN FILMS PREPARED BY PULSED LASER DEPOSITION, M. Cazzanelli, D. Cole and J.G. Lunney, Trinity College, Dublin 2, Ireland; K.P. O'Donnell, P.G. Middleton, C. Trager-Cowan, University of Strathclyde, Scotland; C. Vinegoni and L. Pavesi, INFN and Dipartimento di Fisica, Università di Trento, Povo (TN), Italy
The luminescent properties of GaN thin films grown by pulsed laser deposition have been studied with the aim of understanding the nature of the luminescent centres and the emission dynamics. The films were grown on heated sapphire substrates using KrF excimer laser ablation of GaN in reactive atmospheres of nitrogen or ammonia.
At low temperature the continuous wave (CW) blue luminescence of the samples grown in nitrogen shows two sharp lines. These lines are attributed to excitonic recombination localized at extended defects, as previously reported by C. Wetzel et al. (Appl. Phys. Lett. **68** (18), 2556 (1996)). Time resolved photoluminescence at room temperature shows a decay profile that can be described with two time constants of about 2.7 ns and 8.2 ns at room temperature. An analysis of the temperature dependence of photoluminescence attempts to assess the relative contributions of radiative and non-radiative recombination in the centres responsible of these emissions. The short time constants support the excitonic attribution of the luminescence.
- L-II/P9** LATTICE DYNAMICS OF BORON NITRIDE, H.W. Leite Alves, J.L.A. Alves, DCNAT-FUNREI, CP 110, 36.300-000 Sao Joao del Rei, MG, Brazil, J.L.P. Castineira and J.R. Leite, DFMM-IFUSP, CP 66318, 05389-970 Sao Paulo, SP, Brazil
Using the density-functional theory within the Full-Potential Linear Augmented Plane Wave method (FP-LAPW), we have calculated ab initio the equation of state and the principal phonon modes in cubic Boron Nitride, including their pressure dependence and the amplitude of the eigendisplacements. A good agreement with the experiment is obtained, whenever a comparison is possible: in fact, most of the results are predictions. A 10-parameter Valence Overlap Shell Model is then constructed from the available experimental data, which are completed by the data obtained in the first-principle calculations: frozen phonon frequencies and eigenvectors. The previous speculations about the anomalous behavior of the effective charge in some Boron compounds and Nitrides are discussed in the context of the present results.
- L-II/P10** THEORETICAL LEED PARAMETERS FOR THE ZINC-BLEND GaN(110) SURFACE, H.W. Leite Alves, J.L.A. Alves, DCNAT-FUNREI, CP 110, 36.300-000 Sao Joao del Rei, MG, Brazil, and J.R. Leite, DFMM-IFUSP, CP 66318, 05389-970 Sao Paulo, SP, Brazil
We present a theoretical study of the equilibrium atomic structure of the GaN(110) surface based on accurate, parameter-free, self-consistent total-energy and force calculations using the density-functional theory (the Full-Potential Linear Augmented Plane-Wave method and Pseudopotential methods associated to the slab supercell model) and ab initio theoretical quantum chemistry theories (the Gaussian92 code associated to the molecular cluster model). From the results we extract the parameters Δ_1 , Δ_{1x} , $\Delta_{2\perp}$, $d_{1\perp}$, $d_{12\perp}$, and ω , as defined by Duke [1] for the (110) surface, to be compared with experimental low energy electron diffraction (LEED) analysis. We analyze the changes in the bond-lengths and the bond-angles at the anion and the cation sites. The driving mechanism for the atomic rearrangement is that under the coordination conditions at the surface the Ga atom prefers a more planar sp^2 -like bonding situation with its three N neighbours and the N atom prefers a p-bonding with its three Ga neighbours.
[1] C. B. Duke and A. Paton, Surf. Sci. **164**, L797(1985).
- L-II/P11** POLARITY SELECTIVE LATERAL PHOTOELECTROCHEMICAL ETCHING OF GaN, Taek Kim and Taeil Kim, Photonics Semiconductor Lab., Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Korea
Since the first demonstration of the photoelectrochemical etching of n-GaN by Minsky et al using KOH and HCl solutions and HeCd (325 nm) laser illumination, much progress has been made by Youtsey et al.. According to the previous studies, polarity selective etching is possible because of different band bending at the GaN/electrolyte interface.
We have studied a polarity selective lateral photoelectrochemical etching of GaN. The etching was conducted with or without an external bias in the a solution under Hg lamp illumination. We have found that the etched side wall profile was changed from a vertical to a negative slope as the etch time increased. It was also affected by the thickness of n-GaN and doping level of n-, and p-GaN. This was due to the hole swapping to the junction side rather than to the surface in n-GaN. This result suggested that there was a critical thickness to be etched depending on the carrier concentrations.
Valence band spike at the heterojunction in p-AlGaIn/n-GaN was found to be effective in preventing the hole swapping to the junction side and making the side wall vertical.
Comparative results obtained by varying parameters such as U.V intensity, solution concentration and the type will be discussed.
- L-II/P12** EFFECT OF Si DOPING ON STRUCTURAL AND ELECTRONIC PROPERTIES OF GaN, N. Shmidt, A. Lebedev, W. Lundin, B. Pushnyi, V. Ratnikov, T. Shubina, A. Tsatsul'nikov, A. Usikov, Ioffe Physico-Technical Institute, St. Petersburg, 194021 Russia, and G. Pozina, B. Monemar, University of Linköping, 581 83 Linköping, Sweden
Recently it has been speculated that Si doping of GaN results in a decrease in dislocation density. In this paper we prove this experimentally, and also demonstrate that a moderate Si-doping improves some electro-physical properties of GaN epilayers.
GaN specular epilayers are grown on (100) sapphire substrates by low pressure MOCVD. The structural study of the samples is done by XRD, SEM and AFM. Electrical properties are characterized by Hall and C-V measurements. Low temperature (2 K) PL measurements are performed in a wide spectral region. Besides the anticipated raise in electron concentration (from $2 \times 10^{17} \text{ cm}^{-3}$ to $7 \times 10^{18} \text{ cm}^{-3}$), an increase in silane flow results in an enhancement of electron mobility from $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Simultaneously, the density of micropipes drops to the point of complete disappearance. Furthermore, we observe a Si-doping induced reduction in contamination by residual transition metals (detected by near-infrared PL spectroscopy) and a decrease in the value of elastic stress.

SYMPOSIUM L

- L-II/P13** SURFACE PHOTOVOLTAGE SPECTROSCOPY AND DEEP LEVEL TRANSITIONS IN GaN, I. Shalish, L. Kronik, Y. Shapira, Y. Rosenwaks, Tel-Aviv University, Ramat Aviv 69978, Israel, U. Tisch and J. Salzman, Technion, Haifa 32000, Israel
Deep levels in unintentionally doped GaN films were studied using Surface Photovoltage Spectroscopy (SPS). The response time in surface photovoltage upon illumination is ~ 600 s. and the relaxation after illumination switch-off is $\sim 5 \cdot 10^4$ s. These transients are similar to those found in persistent photoconductivity in GaN. In MOCVD grown films with low temperature AlN buffer layers, two defect states, situated at 1.3 eV and 2.7 eV above the valence-band were found. The former is identified as the cause of yellow luminescence in GaN. The results indicate that the yellow luminescence is due to capture of conduction-band electrons (or electrons from very shallow donors) in the gap state, which seems to be related to grain boundaries. The gap state photovoltage signal is considerably lower in GaN grown on low temperature GaN buffer layers.
- L-II/P14** OPTICAL STUDIES OF THE CORRELATION BETWEEN BANDGAP FLUCTUATION, STOKES-LINE SHIFT AND OPTICAL GAIN IN GaN/InGaN QW's, G. Bahir, Technion, Haifa 3200, Israel; D. Cohen, A. Abare, L. Coldren, S. Denbaars, University of California Santa Barbara, Santa Barbara CA 93106, USA
Emission mechanisms of quantum well GaN/InGaN structures with various well widths and bulk three dimensional InGaN were investigated. Samples used in this study were grown on sapphire (0001) substrates by metalorganic vapor epitaxy (MOVPE) with low temperature GaN buffer layers. Bandgap fluctuations in InGaN can be monitored by using differential absorption spectroscopy (DAS). By comparing photoluminescence with absorption we measured Stokes-shift in several samples. The net modal gain was measured by using variable excitation strip length (VEL) optical pumping method. The InGaN layers showed potential (bandgap) fluctuations, which are probably due to compositional inhomogeneity and/or monolayer fluctuations. Our results seem to indicate that certain amount of bandgap fluctuations in the InGaN QW's maximizes the gain and increases the Stokes-shift. The spontaneous and stimulated emission from undoped InGaN QW's was assigned to the recombination of excitons, localized at the potential minimum. The improvement of the emission intensity may be attributed to the increased of exciton binding energy (E_{ex}) of localized excitons in the QW's.
- L-II/P15** OPTICAL ANISOTROPY IN GAN GROWN ON A-PLANE SAPPHIRE, A. Alemu, J. Campo, M. Julier, B. Gil and J. Lascaray, Groupe d'Etude des Semiconducteurs, CC074, Université de Montpellier II, Place Eugene Bataillon, 34095 Montpellier, France; S. Nakamura, Nichia Chemical, Anan, Japan
GaN epilayers grown on A-plane sapphire undergo an orthorhombic strain field giving an in-plane anisotropy of the optical response. By varying the polarization conditions of reflectivity measurements, we obtain both the in-plane anisotropy of the strain field and the values of the last unknown deformation potentials. Second from a very careful lineshape fitting of the reflectivity spectra, we obtain the splittings between Γ_2 and Γ_4 excitons and report the first determination of the electron-hole exchange energy in GaN: 0.6 ± 0.1 meV. This value is compared to the data obtained for other III-V and II-VI semiconductors, taking into account of the length of the chemical bonds and the variations of the dielectric constant.
- L-II/P16** THERMAL STABILITY OF WSi_x OHMIC CONTACTS ON GaN, S.J. Pearton, S.M. Donovan and C.R. Abernathy, Department of Materials Science and Engineering, University of Florida, Gainesville FL 32611, USA; F. Ren, Department of Chemical Engineering, University of Florida, Gainesville FL 32611, USA; J.C. Zolper, Office of Naval Research, Arlington VA 22217, U.S.A.; M.W. Cole, US Army Research Laboratory, WMRD, Aberdeen Proving Ground Maryland 21105, USA; A. Zeitouny and M. Eizenberg, Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel; and R.J. Shul, Sandia National Laboratories, Albuquerque NM 87185, USA
We have sputter-deposited 500-1200 Å thick $WSi_{0.45}$ metallization onto n⁺ GaN ($n=10^{14} \text{cm}^{-3}$) doped either during MOCVD growth or by direct Si⁺ ion implantation ($5 \times 10^{15} \text{cm}^{-2}$, 100 keV) activated by RTA at 1100°C for 30 secs. In the epi samples R_c values of $\sim 10^{-4} \Omega \text{cm}^2$ were obtained, and were stable to $\sim 1000^\circ \text{C}$. The annealing treatments up to 600°C had little effect on the WSi_x/GaN interface, but the $\beta\text{W}_2\text{N}$ phase formed between 700-800°C, concomitant with a strong reduction (approximately a factor of 2) in near-surface crystalline defects in the GaN. Spiking of the metallization down the threading and misfit dislocations was observed at 800°C, extending $>5,000 \text{Å}$ in some cases. This can create junction shorting in bipolar or thyristor devices. R_c values of $<10^{-4} \Omega \text{cm}^2$ were obtained on the implanted samples for 950°C annealing, with values of $\sim 10^{-5} \Omega \text{cm}^2$ after 1050°C anneals.
- L-II/P17** ELECTRO-OPTICAL CHARACTERIZATION OF h-BN THIN FILM WAVEGUIDES BY PRISM-COUPPLING TECHNIQUE, J. Boudiombo and J.C. Loulergue, Matériaux Optiques à Propriétés Spécifiques*, A. Bath and P. Thevenin, Laboratoire Interfaces Composants et Microélectronique*, *CLOES-Université de Metz et Supélec, 2 rue E. Belin, 57978 Metz Cedex 03, France
Recent interest in non-linear and electro-optical materials for high temperature has been driven by the demand for novel fibre optic and electro-optic devices which can operate in severe environmental conditions. In this way, elaboration and optical characterization i.e the control of waveguide parameters of new material is a prerequisite for tailoring Optical Integrated Circuits (OIC) devices. Boron Nitride is a wide band gap (5.8 eV) and III-Nitride semiconductor material. In thin film form, it presents interesting specific physical properties such as good transparency (UV-IR) and hardness, stability and high acoustical velocity. Therefore, optical coating h-BN thin films with high anisotropy structure have been successfully prepared by Plasma Enhanced Chemical Vapour Deposition (PECVD) and investigated. This graphitic phase of BN is expected to exhibit workable electro-optical and acousto-optical properties which can find applications as switches or SAW. In previous work [1] we have demonstrated the feasibility of optical waveguide in h-BN thin film. In this contribution we present the electro-optical properties of h-BN thin guiding layer. The r_{33} coefficient has been determined from displacement of synchronous angle under an applied dc high voltage by the prism coupling method. For such material elaborated by a micro-wave PECVD process, we found $r_{33} = 5 \text{ pm.V}^{-1}$ for a thickness of $0.85 \mu\text{m}$ with $n_e = 1.7141$ and $n_o = 1.6482$ measured at 632.8 nm .
[1] J. Boudiombo & al., Materials Science & Engineering B46 (1997) 96-98.
- L-II/P18** PHOTOLUMINESCENCE OF PLASMA REMOTE CVD BN FILMS DEPOSITED ON Ge, GaAs AND InAs SUBSTRATES, VI. Belyi and A.A. Rastorguev, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch., Lavrentiev Ave. 3, 630090 Novosibirsk, Russia
There was carried out photoluminescent investigations of BN films ($d \sim 200 \text{nm}$), obtained from borazine ($\text{B}_3\text{N}_3\text{H}_6$) by PR CVD method on different semiconducting materials: Ge, GaAs and InAs slices at $T \sim 500 \text{K}$. The photoluminescence spectra (PLS) were taken at 300K and 77K in the range 250-900nm. Intensive luminescence of the films was displayed in the range of excitation 200-300nm. Typical PLS were consisted of two bands with $\lambda_{\text{max}}^1 = 375 \text{nm}$ and $\lambda_{\text{max}}^2 = 690 \text{nm}$. Cooling down to 77K was led to shift of the bands $\lambda_{\text{max}}^1 \rightarrow 340 \text{nm}$, $\lambda_{\text{max}}^2 \rightarrow 650 \text{nm}$ and rise of emission intensity. The band structure at $\lambda \sim 340 \text{nm}$ became more complicated. Bands position, their intensity, excitation wavelengths slightly differ depending on the substrate material and films synthesis process. PLS of the BN films on the substrates from Ge, GaAs and InAs obtained under the same conditions have different halfwidths, owing to doping of the BN films during the growth processes by substrate materials. The band at $\lambda_{\text{max}}^1 = 375 \text{nm}$ can be attributed to the recombination luminescence in the middle of band-gap of this particular BN films material. So, the photoluminescent method can serve as the sensitive tool for electron structure and technological peculiarities investigations of such the Wide Gap Materials as BN films.

- L-II/P19** **PHOTOLUMINESCENCE OF PLASMA EXCITED CVD Si_3N_4 FILMS DEPOSITED ON Si, Ge, GaAs AND InSb SUBSTRATES**, V.I. Belyi and A.A. Rastorguev, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Lavrentjev Ave. 3, 630090 Novosibirsk, Russia
Photoluminescent spectra (PLS) of Si_3N_4 films, obtained by PECVD technology at 500K, were taken at 300K and 77K in the range 300-1000nm. They differ for $\lambda_{\text{ex}}=245\text{nm}$ and $\lambda_{\text{ex}}=267\text{nm}$ by number of bands, halfwidths and intensity ratios. PLS of the films obtained on different semiconducting substrates at the same conditions do not coincide. Treatment with UV light (Deuterium-hydrogen 400Watt lamp, $\lambda=245\text{nm}$) of $\text{Si}_3\text{N}_4/\text{GaAs}$ specimen was led to the spectra alteration: halfwidths and number of bands were diminished, the luminescence became polarized. We identified the emission bands position with electron transitions between defect levels in the band gap of Si_3N_4 : the silicon dangling bonds ($=\text{Si}^\bullet$), the nitrogen dangling bonds ($=\text{N}^\bullet$) and the $=\text{Si}-\text{Si}=$ units etc and between defect levels and the valence-band top and conduction-band bottom of Si_3N_4 . Variation of the PLS on different semiconductors we explain by doping of Si_3N_4 films with Ge, In, Ga atoms and origin of new phases, for example, GaN.
So, the Photoluminescent method can be successfully used as fine and highly sensitive instrument for control of technology special features and electron structure peculiarities of Wide Gap thin films Materials.
- L-II/P20** **SUBBANDGAP OPTICAL ABSORPTION OF MOVPE GaN GROWN UNDER CONTROLLED NULEATION**, P. de Mierry, H. Lahreche, S. Haffouz, P. Vennéguès, B. Beaumont, F. Omnès, and P. Gibart, CNRS-CRHEA, rue B. Grégory, Sophia Antipolis, 06560 Valbonne, France
Subbandgap absorption is a useful tool to study the defect-related optical transitions in semiconductors. In this study, photothermal deflection spectroscopy (PDS) was used to measure the absorption coefficient in thin GaN epilayers grown on sapphire by MOVPE. The PDS presents several advantages over conventional transmission techniques, among them a higher sensitivity and a quasi insignificant sensitivity to light scattering effects, which can be dominant in non homogeneous layers. Our method is based on the 3D growth of GaN initiated by the in-situ deposition of a thin $\text{Si}_x\text{N}_{1-x}$ film on the sapphire substrate. GaN islands occur and can subsequently coalesce until the formation of an epilayer exhibiting a specular surface and a lower defect density in comparison with GaN films obtained by direct growth on buffer layers. The absorption was measured at different stages of the growth process and was found to be non uniformly distributed in the films. The analysis of the interference fringes in the PDS spectra provided information about the absorption depth profile. A modeling of absorbance on multilayers was compared with the experimental data and confirmed that defects were mainly restricted at the GaN/substrate interface. This interface was also analyzed by Transmission Electron Microscopy (TEM) to elucidate the nature of these defects.
- L-II/P21** **RESPONSIVITY OF GaN and (Ga,Al)N BAND-GAP GRADED ULTRAVIOLET p-n DETECTORS**, M.J. Malachowski, Institute of Physics, Pedagogical University, Al. Armii Krajowej 13/15, 42 201 Czesochowa, Poland
A theoretical study has been carried out on the responsivity of an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (n)-GaN(p) photodiode ultraviolet detector in which the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer has an energy band-gap grading. To perform the calculation a quasi-analytical solution to the one-dimensional continuity equation was used which includes the spatial dependency of the material properties, such as the absorption coefficient and the band gap of the band-gap graded n-type layer of the photodiode. In the calculations the average values of the minority carrier diffusion length and lifetime determined from a homogeneous n-p GaN photodiode were used. Since a moderate grading is considered this seems to be justified. The effect of n-type front layer thickness and surface recombination rate of energy band-gap graded photodiodes on the responsivity was analyzed and compared to that of the ungraded photodiodes. Compared to ungraded photodiodes an enhanced current responsivity and its much reduced dependence on graded layer thickness and on the surface recombination rate are found.
- L-II/P22** **THE AlN SURFACE: A PHOTOELECTRON SPECTROSCOPY STUDY**, T. Wrase, P. Reinke, P. Oelhafen, Institut für Physik, University of Basel, Klingelbergstr.82, 4056 Basel, Switzerland, and P.K. Bachmann, H.-P. Loebl, Philips Research Laboratories Aachen, Weissshausstr. 2, 52066 Aachen, Germany
Thin AlN films were grown on Si(111) substrates by dc magnetron sputtering and by electron beam evaporation with various manufacturing parameters. The surface was modified through heating up to 1200°C, a hydrogen plasma treatment and oxygen ion irradiation. The changes in the electronic structure of the surface were monitored in situ by photoelectron spectroscopy in the x-ray (XPS) and ultraviolet (UPS) regime.
Special attention is paid to the modification of the AlN surface in order to achieve a negative electron affinity. We will discuss the influence of impurities and surface composition on the electronic properties and the negative electron affinity in particular.
- L-II/P23** **THE EMISSION SPECTRUM OF PULSED LASER DEPOSITED GaN AND ITS POWDER PRECURSOR**, K.P. O'Donnell, P.G. Middleton, C. Trager-Cowan, University of Strathclyde, Scotland and D. Cole, M. Cazzanelli, J.G. Lunney, Trinity College, Dublin, Ireland
Pulsed laser deposition (PLD) offers a fast and convenient route for preparing crystalline GaN thin films that may be used either directly in devices or as substrates for conventional growth. Thin films of wurtzite GaN have been grown on heated sapphire substrates in reactive atmospheres of nitrogen or ammonia by pulsed laser deposition (PLD) using KrF excimer laser ablation of compressed and sintered powder targets of GaN. We report here a comparative study of PLD films and their powder precursor by means of low temperature photoluminescence (PL) spectroscopy, cathodoluminescence (CL) imaging and scanning electron microscopy (SEM).
GaN powder manufactured by Cerac Inc. shows several well-defined PL features. Although the free exciton is absent, two relatively sharp bands appear at 3.461 eV and 3.410 eV, in addition to the familiar donor-acceptor pair band near 3.2 eV and the well-known yellow band. SEM imaging reveals relatively poor crystallinity in the micropowder.
PLD films prepared from the Cerac powder show a completely different set of sharp features, between 3.360 eV and 3.160 eV. Thus it is clear that PLD is not just a means of stoichiometric material transfer, but also leads to modification of structural and electronic properties. The spectroscopy of these sharp lines, observed previously in GaN samples prepared by vapour phase epitaxial techniques, provides some interesting clues to their origin.
- L-II/P24** **THE OPTICAL AND STRUCTURAL PROPERTIES OF InGaN EPILAYERS WITH VERY HIGH INDIUM CONTENT**, P.G. Middleton, K.P. O'Donnell, C. Trager-Cowan, University of Strathclyde, Scotland; S.C. Bayliss, A. Sapelkin, De Montfort University, England and W. Van Der Stricht, I. Moerman, P. Demeester, IMEC-INTEC, University of Gent, Belgium
The ability to grow high quality InGaN material with a wide range of indium concentrations is essential if the nitrides are to reach their full-spectrum device potential. While efforts in the area of low-concentration InGaN-based devices have proved extremely fruitful in recent years, the growth of InGaN layers with high indium fractions remains a challenge. Recent investigations into anomalies in the optical linewidths and spatial homogeneity of both alloy epilayers and devices have highlighted the need to improve our understanding of these materials if nitride devices are to compete successfully at the red end of the visible spectrum.
In this paper, we present the results of optical and structural investigations of MOVPE-grown InGaN layers with high indium molar fraction. Absorption and microphotoluminescence spectra allow us to readily identify regions of varying Indium content in the range 50-100% in selected samples. High resolution energy dispersive X-ray analysis (EDX), coupled with scanning electron microscopy and cathodoluminescence imaging, allow us to determine the correlation between optical and structural properties on the nanoscale in such samples.
Finally, extended X-ray absorption fine structure (EXAFS) at the In and Ga K-edges reveals how a rich structure on the atomic scale varies with the mean Indium/Gallium ratio.

- L-II/P25** ION BEAM SPUTTER ETCHING OF GALLIUMNITRIDE GROWN BY CHLORIDE TRANSPORT LP-CVD, M. Topf, F. Cavas, and B.K. Meyer, I. Physikalisches Institut, Universitaet Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany; B. Kempf, Deutsche Telekom Forschungs- und Technologiezentrum, Kavallerie Süd 3, 64276 Darmstadt, Germany and P. Veit, Institut fuer experimentelle Physik, Otto-von-Guericke Universitaet, Uni-Platz 2, 39106 Magdeburg, Germany

Gallium(III)-chloride and ammonia were used as precursors for the growth of GaN epilayers on sapphire and 6H-SiC. The total gas pressure during growth was about 0.5 mbar. Growth rates between 2 and 6 $\mu\text{m/h}$ have been achieved for different V/III ratios. For the determination of the optical, structural and electrical properties of all layers low temperature PL, XRD in the $\omega/2\theta$ mode and Hall measurements were used as standard characterization methods.

These GaN layers grown by chloride transport LP-CVD were etched by ion beam sputter etching with carbondioxide. Before etching all samples were masked by e-beam evaporated titanium. We report on the dependence between the etchrate in GaN and the angle of ion beam incidence. Furthermore we present structural examinations of the surfaces before and after ion etching as well as an analysis of masking effects. Therefore the samples were investigated with respect to surface roughening and structural defects by optical microscopy, SEM and TEM.

- L-II/P26** LOCAL STRUCTURE AND PHOTOLUMINESCENCE OF GaN POWDER PREPARED BY METATHESIS, S.C. Bayliss, S.M. Clark*, A. Sapelkin, A. Filatov, I. Fletcher, R. Jones*, Solid State Research Centre, De Montfort University, Leicester, UK; *Daresbury Laboratory SRS, Warrington WA4 4D, UK

GaN and its alloys with In and Al form the basis of exciting optoelectronic devices including uv/vis LEDs and lasers, but the mechanism for light emission is not fully understood. There are many indications that the emission is linked to the particular micro- or nanocrystallite structure i.e. hexagonal or cubic, but it is possible that defects such as step dislocations or even chemically disordered regions are involved. Last year high pressure solid state metathesis of GaN powder was demonstrated as an alternative preparation method for light emitting GaN. We have investigated the photoluminescence and local structure of GaN powder prepared under different synthesis conditions, and after post-processing. The metathesis and post-processing pressure was varied up to 60 kbar and the temperature from 77 to 1300K, and x-ray diffraction (xrd), Ga and N K-edge x-ray absorption fine structure (exafs), and PL investigated. The micro- and nanostructure from electron microscopy, and corresponding cathodoluminescence maps, are discussed in terms of the local and long range order determined from the xrd and exafs. Finally we consider the interrelationship between the optical and structural properties of GaN powder from x-ray excited optical luminescence.

- L-II/P27** PROPERTIES OF STRAINED AND UNSTRAINED III-NITRIDES, J.-M. Wagner, K. Karch, and F. Bechstedt, Friedrich-Schiller-Universitaet Jena, Institut fuer Festkoerpertheorie und Theoretische Optik, Max-Wien-Platz 1, 07743 Jena, Germany

We present results of first-principles calculations of structural, dielectric, and lattice-dynamical properties of the group-III nitrides BN, AlN, and GaN. We consider both polytypes, the zinc-blende and the wurtzite structure, in the strain-free case and under hydrostatic pressure. The calculations within density-functional theory and local-density approximation are based on soft pseudopotentials and plane waves.

We determine the Born effective charges, the high-frequency dielectric constants, and the zone-center phonons. In all cases the Born effective charges and the high-frequency dielectric constants decrease with rising hydrostatic pressure. The LO-TO splittings do not exhibit a unique trend. For AlN and GaN they increase with increasing pressure, whereas the converse holds for BN.

All zone-center optical phonon frequencies increase with increasing hydrostatic pressure, except for the lower E_2 modes of wurtzite AlN and GaN. The mode Grüneisen parameters as well as the pressure coefficients of the Raman-active modes are in reasonable agreement with the experimental findings. The mode softening, indicated by the negative, Grüneisen parameter of the lower E_2 modes, may be interpreted as a precursor of the pressure-induced transition into the rocksalt phase.

- L-II/P28** A TUNABLE BLUE LIGHT EMISSION OF InGaN/GaN QUANTUM WELL THROUGH THERMAL INTER-DIFFUSION, E. Herbert Li, M.C.Y. Chan, and E.M.T. Cheung, University of Hong Kong, Department of Electrical and Electronic Engineering, Pokfulam Road, Hong Kong

In recent years, blue light emitting diodes and lasers of III-nitride semiconductors are of much interest. This is mainly due to its large bandgap ranged from 1.89eV (wurtzite InN) to 3.54eV (wurtzite GaN). InGaN/GaN quantum well (QW) structures have been used to achieve high lumens blue LEDs. In this paper, InGaN/GaN QW intermixing structure is theoretically analyzed and which is used to optimize and tune the optical emission. The QW composition intermixing is a thermal induced interdiffusion of the constituent atoms (In and Ga) through the hetero-interface. The intermixed structures are thermally induced by thermal annealing processes. In this paper, we will present the band structure of strained InGaN/GaN single QW under the influence of interdiffusion. Band structure is a fundamental aspect in determining the electronic and optical properties of the materials such as absorption and emission. In the model, the diffusion process is modeled by Fick's second law, and the 6x6 multi-band effective-mass Hamiltonians, based on the theory of Luttinger-Kohn and Pikus-Bir, are used to calculate the band structure of hexagonal-type (wurtzite) GaN quantum well. Band structure parameters derived using the full potential linearized augmented plane wave method within the local density approximation is used to calculate the valence-band structure of the QW.

- L-II/P29** PHOTOASSISTED ANODIC ETCHING OF GaN FILMS IN NaOH ELECTROLYTE WITH CL IONS, M. Ohkubo, A. Hashimoto and A. Yamamoto, Faculty of Engineering, Fukui University, 3.9.1 Bunkyo, Fukui, 910-8507, Japan

Photo-assisted anodic etching, of high quality n-GaN films grown by metalorganic chemical vapor deposition (MOCVD) on sapphire substrate using a sodium hydroxide (NaOH) electrolyte at room temperature is reported on. It is important in the use of electrolytic etching techniques using a NaOH electrolyte that the formation of a gallium hydroxide layer on the GaN films surface be prevented. For the NaOH electrolyte without chloride ions, gallium hydroxide are left on the surface, resulting in anodic current density decreasing. It is found that the addition of chloride ions in the NaOH electrolyte accelerates the rate of photo-assisted anodic etching of GaN films. The etching rate is increased by increasing the anodic current density. The effect of adding chloride ions in the electrolyte is to reduce the amount of gallium hydroxide formed on the GaN surface. It seems that the presence of chloride ions in the NaOH electrolyte plays an important role in the photo-assisted anodic etching of n-GaN films.

- L-II/P30** OBSERVATION OF ORDERING AND PHASE SEPARATION IN $\text{In}_x\text{Ga}_{1-x}\text{N}$ LAYERS GROWN BY MOVPE, P. Ruterana, F. Deniel, Laboratoire d'Etudes et de Recherches sur les Matériaux, UPRESA CNRS 6004, Institut Sciences de la Matière et du Rayonnement, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

The growth InGaN layers is still not well controlled due to the difficult incorporation of Indium.

Until now results have been published concerning the phase separation which was mainly supposed to give rise to the formation layers made of InN and GaN patches. This was tentatively explained by the fact that these two compounds have a large mismatch (~10%).

In fact, it is now being seen that the growth of InGaN can lead to the formation of a ternary alloy, InN and GaN, In and GaN, and finally in some cases a new ternary ordered alloy. This means that depending on the growth condition one may obtain a combination of the four cases, along with the characteristic crystallographic defects.

In this work, we have been investigated, by conventional and analytical microscopy, InGaN layers grown by MOCVD in order to characterize the indium incorporation and the incidence on the microstructure of the epitaxial layers.

SYMPOSIUM L

- L-II/P31** ELECTROLUMINESCENT SPECTRA OF LEDs BASED ON AlGaIn/GaN-HETEROSTRUCTURES WITH MQWs, V.E. Kudryashov, A.N. Turkin, A.E. Yunovich, Moscow State Lomonosov University, 119899 Moscow, Russia; M. Koike, Toyoda Go.Co., 1 Nagahata, 452, Japan
Spectra of blue LEDs based on AlGaIn/GaN-heterostructures with MQWs (5 InGaIn/GaN, [1]) were studied in a range of currents $J=0.15$ μ A-150 mA. Spectral maximum shifts with J in the interval 2.5-2.7 eV; spectra are exponential on lower and higher sides of energy. Spectra are approximated by a model of radiative recombination in the 2D-active layer, taking into account tails in the joint density of states and a degree of filling of the states near the band edges [2]. Parameters of the model: effective energy gap E_g^* , and an exponent describing the long-wavelength tail E_0 # 55-59 meV (determined by potential fluctuations) are discussed. The temperature T in the active region was determined from the higher energy exponent; T was ≈ 380 K at 100 mA.
[1] M. Koike, N. Koide, S. Asami, J. Umezaki, S. Nagai, S. Yamasaki, N. Shibata, H. Amano, I. Akasaki. Proc. of SPIE-Intern. Soc. Opt. Engin., v. 3002, 1997.
[2] K.G. Zolina, V.E. Kudryashov, A.N. Turkin, A.E. Yunovich. Semiconductors, v.31, N 9, p. 901.
- L-II/P32** AB INITIO PSEUDOPOTENTIAL STUDY OF ELECTRONIC AND STRUCTURAL PROPERTIES IN GaN, A. Zaoui, M. Certier, O. Pagès, M. Ferhat and H. Aourag*, Université de Metz, L.S.O.M., 8 rue Marconi, Technopole 2000, 57078 Metz Cedex 3, France; *Computational Materials Science Laboratory, Physics Department, University of Sidi-Bel-Abbes, 22000, Algeria
The structural and electronic properties of cubic GaN are studied by solving the self-consistent Kohn and Sham equations, in the framework of density functional theory (DFT) using the local density approximation (LDA). The orbitals are expanded in a plane wave basis set and the cores are described by norm conserving pseudopotentials. We compute the total energy, the band structure and the electronic charge density. Calculations of the lattice constant, the bulk modulus and the elastic constants are also given. The analysis of the charge density, bonding properties and band structure show the influence of d electrons in GaN. The results are in good agreement with the previous ones.
Key words: Density functional theory (DFT)-Local Density Approximation (LDA)-Pseudopotentials (PP)-Band structure-elastic constants.
- L-II/P33** DOPING OF Al_xGa_{1-x}N ALLOYS, C. Stampfl and J. Neugebauer, Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin-Dahlem, Germany; C.G. Van de Walle, Xerox PARC, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA
Most electronic and optoelectronic device structures require n- and p-type doping of Al_xGa_{1-x}N alloys. Experimental results indicate that doping efficiencies in Al_xGa_{1-x}N are lower than in GaN; in this paper we address the cause of these doping difficulties, based on results from first-principles density-functional-pseudopotential calculations. For n-type doping we find that oxygen (the most common unintentional donor) exhibits a DX transition which converts the shallow donor into a deep level when $x > 0.3$. Silicon donors do not exhibit this transition. All donors, however, experience increased compensation by cation vacancies (triple acceptors) with increasing alloy composition x . For p-type doping we find that the doping efficiency decreases due to increased compensation by nitrogen vacancies. We also calculate an increase in the magnesium ionization energy with increasing x . We have performed a comprehensive investigation of alternative acceptor impurities; none of the candidates exhibits characteristics which surpass those of Mg in all respects. Only beryllium emerges as a potential alternative dopant, though it may suffer from compensation by Be interstitial donors.
- L-II/P34** Last minute poster from UCSB, Milan Singh Minsky, ECE Dept., University of California Santa Barbara, USA

E-MRS'98 SPRING MEETING



SYMPOSIUM M

Molecular Photonics for Optical Telecommunications: Materials, Physics and Device Technology

Symposium Organizers

- | | |
|----------------------|--|
| J. ZYSS | France Telecom/CNET, Bagneux and ENS Cachan, LPQM, Cachan, France |
| F. GARNIER | CNRS, Labo. des Matériaux Moléculaires, Thiais, France |
| V. AGRANOVICH | Institute for Spectroscopy, Troitsk, Moscow obl., Russia |

The assistance provided by

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is acknowledged with gratitude.

(Germany)

SYMPOSIUM M

Tuesday, June 16, 1998

Mardi 16 juin 1998

Morning

Matin

SESSION I

Chairperson: P.N. Favennec

M-I.1 8:30-9:15 - Invited - **OVERVIEW OF POLYMERS FOR COMMUNICATIONS, G.I. Stegeman**, CREOL, Un. Central Florida, 4000 Central Florida Blvd., Orlando FL 32826-2700, USA
Polymers have been developed by chemists, materials scientists, physicists and engineers into a very viable material class for a number of applications in optical communications in particular, and photonics in general. Advances, especially in materials science have been very rapid in the last few years and a number of polymeric devices have been designed, fabricated and tested based on prototype materials. This has provided feedback into the materials and processing engineering communities, resulting in further improved materials. Currently polymeric devices are challenging and have in isolated cases exceeded some performance characteristics of the more established materials such as semiconductors and ferroelectrics. An excellent example is the > 100 GHz bandwidth achieved with polymeric electro-optic modulators. Significant research efforts still need to be invested before these highly promising prototype devices mature into large scale practical uses, and many challenging material and processing problems still need to be investigated further and solved. These will be discussed in this tutorial and the parameters needed for further progress will be identified.

M-I.2 9:15-10:00 - Invited - **POLYMER OPTICAL FIBERS FOR TELECOM, K. Sasaki**, Keio University, Yokohama, Japan

M-I.3 10:00-10:45 - Invited - **DESIGN AND FABRICATION OF ELECTRO-OPTICAL POLYMER MODULATORS AND SWITCHES, R.M. de Ridder, A. Driessen**, E. Rikkers, P.V. Lambeck and M.B.J. Diemeer*, MESA Research Institute, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands; *Akzo Nobel Central Research, PO Box 9300, 6800 SB Arnhem, The Netherlands

Integrated optics devices based on silicon and its oxides exhibit attractive properties as long as only passive functions are considered. For active functions like electro-optical modulation and switching, different materials have to be added. Promising candidates are polymers with a high electro-optical coefficient as they can be combined/integrated with several passive materials. Electro-optical interaction can be exploited for obtaining modulation or switching in polymer-based devices using several principles (e.g. Mach-Zehnder, Digital Optical Switch, tuned coupling to surface plasmons), which have been investigated and tested using different materials. We compare these principles in view of several aspects of practical importance: realistic values of electro-optical coefficients and wavelength-dependent attenuation, optical, electrical and chemical compatibility of substrate, guiding and cladding layers, channel definition by etching (inverted) ridge waveguides or by photo-bleaching, local and global poling methods, polarisation-dependence, and the design of efficient high-bandwidth travelling wave electrodes. We will discuss the practical difficulties encountered and show the obtained results with phase- and intensity modulators and switches.

10:45-11:15

BREAK

SESSION II

M-II.1 11:15-12:00 - Invited - **INTERFACE MOLECULAR ENGINEERING FOR THIN FILM TRANSISTORS, Yue Kuo**, IBM T.J. Watson Research Center, Yorktown Heights, NY 10598, USA

Thin film transistors (TFTs) have been widely used in microelectronic products, such as active matrix liquid crystal displays, 2D imagers, dynamic random access memory's. TFTs have also shown potential applications in large area optical devices, such as artificial retina and neural network. In spite of the nature of the semiconductor material, i.e., amorphous or polycrystalline silicon, all TFTs have the multilayer structure. The transistor performance is greatly contributed by a thin layer, i.e., about 200Å, of current path at the interface of the semiconductor and the gate dielectric films. For the large area TFT fabrication, all major thin film layers are deposited by the plasma enhanced chemical vapor deposition (PECVD) method. A drastic variation of the interface characteristics is often observed, which is due to the non-equilibrium process nature of PECVD. In this paper, the author is going to discuss molecular-level issues, i.e., chemistry, morphology, stress, and plasma radiation, in this critical interface area of the TFT. Examples on the TFT characteristics change with the variation of above parameters will be given. At the conclusion, the author will rationalize many conflict results reported in the literature according to the interface molecular engineering principle.

M-II.2 12:00-12:45 - Invited - **DEVICE PERFORMANCE AND APPLICATIONS OF POLYMER LIGHT-EMITTING DIODES, R.E. Gill**, P. van de Weijer, H.F.M. Schoo, C.T.H. Liedenbaum, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

In comparison to competing thin film display technologies polymer light-emitting diodes offer important advantages like high efficiencies, low operating voltage, good viewing angle, colour tuning via adjustment of the chemical structure and easy processing into large area devices via spin coating. In order to become commercially successful, the basic technology has to offer opportunities for flat display options and lifetimes of devices have to meet the requirements of the various applications. An overview of the technological progress made at Philips concerning materials, processing and device fabrication of light-emitting diodes based on fully conjugated PPV-type polymers will be presented.

12:45-14:00

LUNCH

Tuesday, June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION III

Chairperson: A. Driessen, MESA Research Inst., Univ. of Twente, Enschede, The Netherlands

- M-III.1** 14:00-14:45 - Invited - HIGH EXCITATION DENSITIES IN OPTICALLY AND ELECTRICALLY EXCITED CONJUGATED POLYMER STRUCTURES, G.J. Denton, N.T. Harrison, N. Tessler and **R.H. Friend**, Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 0HE, UK
- Conjugated polymers such as poly(p-phenylenevinylene), PPV, show efficient luminescence, either optically or electrically stimulated (the latter in electroluminescent diodes). There has been rapid progress in the development of optically-pumped structures which show stimulated emission and associated line-narrowing. We present measurements on a range of devices which show sufficient feedback to demonstrate lasing, and we discuss criteria for reducing the lasing threshold. We also present measurements of high peak brightness polymer LEDs, which can show current densities of up to 1000 A/cm², and peak brightnesses up to 5 Mcd/m². These devices show clear evidence for increased carrier mobilities at high charge injection densities.

- M-III.2** 14:45-15:30 - Invited - POLYMER LIGHT EMITTING DIODES: NEW MATERIALS AND DEVICES, **Z. Bao**, Z. Peng, J. A. Rogers, A. Dodabalapur, M.E. Galvin*, Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, NJ 07974, USA, *Department of Materials Science, University of Delaware, Newark, DE 19716, USA
- Single layer polymer LEDs are ideal candidates for practical applications due to their easy processing conditions. However, low quantum efficiency of light generation is often obtained due to imbalanced charge injection and transport of holes and electrons. In this paper we report new conjugated polymers with electron deficient oxadiazole moieties as side-chains and in the polymer backbone. These polymers have shown at least an order of magnitude increase in electroluminescence efficiencies and better charge injection properties compared to their corresponding conjugated backbone polymers. In addition, novel patterned LED device structures which emit in geometries with features into the sub-micron range will be presented. Finally, issues regarding integration of polymer transistors with organic LEDs will be discussed.

- M-III.3** 15:30-16:00 STRONG EXCITON-PHOTON COUPLING IN ORGANIC MICROCAVITIES, **D.G. Lidzey**, D.D.C. Bradley, M.S. Skolnick, T. Vergili, S. Walker, Department of Physics, The University of Sheffield, Hounsfield Road, Sheffield S3 7RH, UK
- We present the first observation of strong coupling between the confined optical field within a microcavity and a molecular exciton absorption band. We have used 2,6 tetra(tert-butyl)phenol-porphine zinc [4TBPPZn] as the active material in the microcavity, selected on account of its narrow absorption linewidth (87 meV). Our microcavities were fabricated by depositing a layer of polystyrene / 4TBPPZn blend between a metallic and a dielectric mirror. At room temperature, by angle tuning, we observe clear Rabi splitting with an anticrossing between the cavity mode and the molecular absorption band. The Rabi splitting can be readily varied by controlling the molecular oscillator strength via the proportion of 4TBPPZn incorporated into the blend, with observed splittings up to 140 meV. Our results are of interest for the study of light-matter interactions in confined structures, and also in the context of recently proposed hybrid organic-inorganic exciton devices and microcavity lasers.

16:00-16:30

BREAK

SESSION IV

Chairperson: N. Ostrowski, Université de Nice, France

- M-IV.1** 16:30-17:00 TWO-LAYER ORGANIC LEDs USING DYE-DOPED PVK AND EVAPORATED SMALL MOLECULES, **L. Berthelot**, J. Tardy, M. Garrigues, J. Joseph and B. Masenelli, LEAME (UMR CNRS 5512), Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France
- This paper reports on the fabrication and on the characterization of LEDs consisting of two layers: a spin-coated PVK layer acting as a hole transport layer which is doped with conventional laser dyes (coumarin or DCM-II) and an evaporated tris(8-hydroxy) quinoline aluminum (Alq₃) acting as an electron injection layer. Luminescence occurred from Alq₃ or the dye depending on the applied voltage. The electroluminescence of these devices was investigated as a function of the nature and the concentration of the dye in the PVK layer and of the thicknesses of respective layers. Alq₃ electroluminescence was clearly visible in room light at V=5 volts corresponding to 0.5 mA/mm².
- The emitting surface was analysed with a lateral resolution as low as 40 μm using Scanning ElectroLuminescence Imaging Microscopy (SELIM), a technique derived from the well known Scanning PhotoLuminescence (SPL) used for semiconductors. This technique was successfully used to assess the homogeneity of the dispersion of dyes as well as the dark spots formation and development.

SYMPOSIUM M

M-IV.2 17:00-17:30

OPTICAL GAIN AT ROOM TEMPERATURE IN PPV-RELATED MATERIALS, N. de la Rosa-Fox*, Optical Sciences Center, University of Arizona, Tucson, AZ 85721, USA

Recently conjugated polymers have been proposed as lasing materials since they combine the optical and electronic properties of semiconductors with the ease of processing and the mechanical properties of polymers. In order to achieve lasing, it is essential to observe optical gain in these materials. By using nanosecond pulses from the second harmonic of a Q-switched Nd:YAG laser (FWHM 6 ns at 10 Hz repetition rate) and the variable stripe length (VSL) method the steady-state luminescence (PL) spectra was measured for various soluble derivatives of Poly(*p*-phenylenevinylene) neat films. The samples were kept at room temperature in vacuum during measurements. The PL spectra feature the vibronic series that is red-shifted from the absorption and shows the characteristic exponential growth with the gain coefficient (100 cm^{-1}). Stimulated emission (SE) largely due to exciton-exciton annihilation are responsible for PL yield, and their blue-shift was side-group dependent. The decrease in the conjugation length improves the gain coefficient. It is resolved the optical gain spectra as well as its shape in a broad spectral range, using moderate injection densities (10^{19} cm^{-3}). The results confirm the potential application of these semiconducting polymers as a new solid-state lasers.

*on sabbatical leave from, Dpto. de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cadiz, 11510 Puerto Real, Cadiz, Spain

M-IV.3 17:30-18:00

OPTICALLY PUMPED POLYMER LASER: GAIN, TUNABILITY, AND COHERENCE, G. Wegmann, H. Giessen, and R.F. Mahrt, Fachbereich Physik und Institut für Physikalische Chemie, Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans Meerwein Strasse, 35032 Marburg, Germany

Conjugated polymers are promising materials in the field of optoelectronics and photonics. Over the last years, there has been considerable effort to achieve lasing from solid conjugated polymers. We report on tunable laser emission from an optically pumped solid π -conjugated polymer blend system placed into an external cavity. We measured the threshold characteristics, the tunability range and the coherence properties of the laser. By means of femtosecond pump-probe spectroscopy we recorded gain spectra and investigated their intensity dependence and temporal evolution. In order to shed light onto the fundamental question concerning the gain mechanism in this class of materials steady-state site selective fluorescence spectroscopy (SSF) is performed on a conjugated polymer with rigid backbone. The observed sharp emission lines off-set from the laser line by the energies of the dominant vibrational modes serves as a seed for the stimulated emission and points towards a description of the optical gain within the well known 4-level mechanism.

Wednesday, June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION V

Chairperson: R.H. Friend, Cavendish Laboratory, Cambridge University, Cambridge, UK

- M-V.1** 14:00-14:45 - Invited - TRANSIENT ELECTROLUMINESCENCE FROM PPV: HOT ELECTRONS AND IMPACT IONIZATION, **D. Davidov**, Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem, Israel
- M-V.2** 14:45-15:30 - Invited - A MODEL OLIGOMER APPROACH FOR SEMICONDUCTING POLYMER MATERIALS, **G. Hadziioannou**, University of Groningen, Department of Polymer Chemistry, Nijenborgh 4, 9747 AG Groningen, The Netherlands
The ultimate goal in our research is the understanding and development of efficient and high-performance Photonic Polymer Materials for Photovoltaic, Electroluminescent, Optical Amplification, and Laser Devices. To achieve this goal, emphasis is put on the understanding of the relation between the molecular structure, the morphology (macro-/microphase separation, crystal structure), the device structure and the photonic properties in conjugated polymers and oligomers. Furthermore, we engineer the Photonic Polymer Materials starting from their synthesis, with which all necessary functionalities for structural and photonic control are introduced by design and judicious choice of the monomers and their respective sequence in the macromolecular chain. Moreover, the nanostructural organization of the macromolecules is controlled by the balance of short and long-range interactions in the Nanostructured Photonic Polymer Materials. The integration in a device configuration affects the functional and morphological behavior of the polymer materials, depending on the device dimensions and the presence of surfaces and interfaces. Key aspect of all the above will be exemplified by the use of two typical materials for photovoltaics and optical amplifiers.
- M-V.3** 15:30-16:00 (TITLE NOT DEFINED), Kouki
- 16:00-16:30 **BREAK**

SESSION VI

Chairperson: D. Davidov, Racah Institut of Physics, Hebrew Univ. of Jerusalem, Israel

- M-VI.1** 16:30-17:15 - Invited - SELF-ASSEMBLED INTERFACIAL LAYERS IN ORGANIC LIGHT-EMITTING DIODES, **L. Zuppiroli**, Laboratoire de Physique des Solides Semicristallins, Département de Physique, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
One of the major challenges in building reliable organic light emitting diodes is to control the inorganic - organic interfaces. A proper engineering of the interface should improve the homogeneity of the interfacial layers and establish ohmic contacts in order to decrease the injection fields and facilitate the balance of electron and hole currents through the device.
In this work we report on Indium-Tin-Oxyde electrodes chemically modified by grafting functionalized electroactive molecules. We show that the surface properties of the oxide can be improved by building such self-assembled monolayers at the interface and that uniform growth conditions of the organic layers can be achieved in this way. We bring also evidence that charge injection from the electrodes can be tuned in such a way that ohmic injection is obtained. This effect is attributed to the permanent electric dipoles brought by the molecules self-assembled into a controlled electric double layer at the interface.
- M-VI.2** 17:15-17:45 UP-CONVERTED STIMULATED EMISSION IN MONOLITHIC ORGANIC SINGLE-CRYSTALS, **V. Dumarcher**, **J.M. Nunzi**, LETI (CEA - Technologies Avancées), DEIN / SPE, Groupe Composants Organiques, Saclay, 91191 Gif sur Yvette, France and **D. Fichou**, Laboratoire des Matériaux Moléculaires, UPR 241 - CNRS, 2 rue Henry Dunant, 94320 Thiais, France
Owing to their anisotropic elongated shape, thiophene oligomers constitute a family of monolithic organic single crystals which are naturally adapted to laser action. Light amplification originates from the combination of a net dipole alignment and of an efficient wave-guiding towards the edges of the ultra-thin crystals. The molecules naturally provide both the emitter and the optical cavity. Microjoule threshold single-photon gain narrowing was observed in a transverse pumping geometry.
Owing to their conjugated π -electron structure, thiophene oligomers also possess a large two-photon absorption cross-section. This particular situation in the world of organic devices permits the achievement of infrared two-photon pumped up-converted stimulated emission with nanojoule-threshold in a longitudinal pumping geometry. In such scheme, polarisation selection is naturally given by molecular order, spectral selection results from efficient gain narrowing and stimulated emission directivity is given by gain-guiding.
- M-VI.3** 17:45-18:15 ORIGIN OF EVOLVED GAS IN ORGANIC LIGHT-EMITTING DIODES, **L.S. Liao**, **J. He**, **X. Zhou**, **X.Y. Miao**, **Z.H. Xiong**, and **X.Y. Hou**, Surface Physics Laboratory, Fudan University, Shanghai 200433, China
Gas evolution from organic light-emitting diodes, caused by Joule heating due to localized electrical shorts in micrometer-sized areas, can be stimulated by thermal treatment. Two kinds of evolved gas in ITO/TPD/Alq₃/Al under thermal treatment are then identified. One is adsorbates on ITO surface during cleaning process, which could form bubbles of about 0.01 mm in size at Alq₃/Al interface when treated at about 100°C. The other is resolved gas from Alq₃, which could form bubbles of more than 0.08 mm in size when temperature is higher than 150°C. In the latter case, the bubble size increases obviously as temperature increases.
Proper surface treatment to ITO could reduce or get rid of the adsorbates and then the smaller bubbles. Purification of Alq₃ could reduce the resolved gas to a certain extent, but could not eliminate the bigger bubbles if there were still localized electrical shorts in the devices or if the devices were under extremely high electrical field.

Thursday, June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION VII

Chairperson: K. Sasaki, Keio University, Yokohama, Japan

M-VII.1 8:30-9:15

TRANSIENT BEHAVIOR OF PHOTOINDUCED ORDERING PROCESSES IN DYE-DOPED POLYMERS, Ahmad El Osman and M. Dumont, Laboratoire Charles Fabry de l'Institut d'Optique, Bât. 503, BP 147, 91403 Orsay Cedex, France

Photoassisted electrical poling and photoinduced anisotropy are efficient ordering methods with photoisomerizable dyes (e.g. azo-dyes cis-trans, or spiropyran-merocyanine photoisomerization). Their efficiency depends on spectral properties of chromophores and on their orientational mobility, in the optical pumping process and in the relaxation process.

We have developed experimental methods and a model for studying the dynamics of the spontaneous rotation of molecules (relaxation towards the thermodynamic equilibrium) and of the photoinduced orientation, when the sample is pumped by a polarized resonant light beam, with or without the presence of a DC electric field. We use the attenuated total reflection method for studying the dynamics of birefringence and of $\chi^{(2)}$. We built a new pump-probe set up for measuring dichroism simultaneously with six probe wavelengths, in order to record the transient behavior of the population and of the anisotropy of both isomeric forms.

We will present new spectroscopic results concerning DR1 and Spiropyran and we will discuss their influence on the mechanisms of photoinduced ordering. With the help of the theoretical model, we demonstrate the role of the reverse photoisomerization (e.g. merocyanine \rightarrow spiropyran).

We will also discuss the orientational relaxation processes, which depend not only on the host material (DR1 is studied in different polymers), but also on the pumping conditions.

M-VII.2 9:15-9:45

PHOTOCONDUCTIVITY STUDIES OF NEW ORGANIC PHOTO-REFRACTIVE MATERIALS, T.K. Däubler and D. Neher, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany, H.-H. Hörhold, Friedrich-Schiller-Universität, Humboldtstr. 10, 07743 Jena, Germany, K. Meerholz, Ludwig-Maximilians-Universität, Sophienstr. 11, 80333 München, Germany

Conjugated polymers have drawn recent attention as photorefractive (PR) materials. Photoinduced changes in the refractive index are caused by redistribution of generated charge carriers. Therefore, charge carrier generation, recombination, transport and trapping are of crucial importance for understanding the fundamentals of the PR effect.

Photoconductivity (PC) experiments are a good tool for studying these phenomena. Poly(arylenevinylene) (PAV) and Poly(vinylcarbazole) (PVK) exhibit notable intrinsic charge carrier generation within the polymer absorption. For PR applications NLO chromophores and sensitizers have to be added. This results in a significant increase of the charge carrier generation efficiency in the long wavelengths range ($\lambda > 633$ nm). The low molecular weight components reduce the glass transition temperature (T_g) depending on the amount and the composition of the additives. Thus, PC experiments on different materials yield valuable information on the relation between photophysical processes and T_g . Experiments performed below and above T_g indicate changes in charge carrier transport, trapping and detrapping which will affect the overall performance of these guest-host materials in photorefractive applications.

M-VII.3 9:45-10:15

ZWITTEWONIC MOLECULES AS DOPING CHROMOPHORES FOR EFFICIENT PHOTOREFRACTIVE POLYMERS, A. Fort, L. Mager, J. Muller, C. Combellas*, G. Mathéy*, A. Thiébault*, IPCMS, Groupe d'Optique Non Linéaire et d'Optoélectronique, 23 Rue du Loess, 67037 Strasbourg Cedex, France, *ESPCI, Environnement et Chimie Analytique, 10 Rue Vauquelin, 75231 Paris Cedex, France

In the last few years, high diffractive efficiencies have been obtained for low glass transition temperature T_g photorefractive polymers doped with push-pull molecules. In addition to the electro optical effect, the ability for the chromophores to move into the polymeric matrix induces a modulation of the refractive index due to the orientational birefringence. This contribution is proportional to the square of the dipole moment and to the linear polarizability anisotropy of the doping molecule. We have studied the efficiency of zwitterionic molecules used as doping chromophores in low T_g photorefractive polymers. The quadratic hyperpolarizabilities and the permanent dipole moments of these molecules are high. However, since their hyperpolarizabilities are negative, the two contributions to the refractive index modulation, i.e. orientational birefringence and electro optical Pockels effects, have opposite signs. We have studied these two contributions for different zwitterionic compounds and we have established the predominant part of the orientational birefringence contribution. The interest of zwitterionic molecules as efficient doping chromophores for low T_g photorefractive polymers has been evidenced.

M-VII.4 10:15-10:45

THIRD-HARMONIC GENERATION AS A SELECTION TOOL FOR ORGANIC MATERIALS FOR NONLINEAR INTEGRATED OPTICS DEVICES, F.C. Blom, A. Driessen, H.J.W.M. Hoekstra, J.B.P. van Schoot and Th.J.A. Popma, MESA Research Institute, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

In the long trajectory from the synthesis of organic nonlinear optical materials to the completed all-optical device it is highly desirable to be able to concentrate already in an early state on a few promising materials. Third-harmonic generation (THG) is a very convenient method as it allows measurements of the third order nonlinear coefficient of very small samples in the liquid and solid state and also of thin films. For our application in all-optical switching devices the relevant parameter is the Intensity Dependent Refractive Index (IDRI). Assuming a simple two-level model for the polymeric materials we can estimate the IDRI on the basis of THG measurements at two fundamental wavelengths and also using the linear absorption of the materials. We have measured the THG of several polymers in the liquid state and as thin film. The nonlinear coefficients and the IDRI are derived and compared with those obtained from other methods by ourselves and from literature. We also briefly show the application of some of these nonlinear materials in all-optical integrated optics devices like a nonlinear Bragg-reflector, Mach-Zehnder interferometer and cylindrical micro-resonators.

10:45-11:15

BREAK

SESSION VIII

Chairperson: G. Stegeman, CREOL, Un. Central Florida, Orlando, USA

M-VIII.1 11:15-11:45

IRRADIATED THICKNESS EFFECTS ON THE LIGHT-EMITTING DEVICES MADE BY ION BEAM ASSISTED DEPOSITION, R. Antony, B. Lucas, B. Ratier and A. Moliton, UMOP, Faculté des Sciences, 123 Av Albert Thomas, 87060 Limoges, France

We have realized light-emitting diodes with an Alq₃ layer. The emissive layer thickness is 75nm and we have assisted the molecular film deposition with an helium ion beam for 4 different positions: 0 to 25nm, 25 to 50nm, 50 to 75 nm and 0 to 75nm.

The ion beam influence on the electroluminescence spectra is negligible but we obtain many differences on the dark current, the luminance and the efficiency versus applied bias characteristics between the 4 LED.

Some teams have realized studies with an ITO anode cleaned with an ion plasma. We have cleaned our ITO anode with an helium ion beam with the same I.B.A.D. parameters. Finally we compare our results obtained with this method and the results obtained by I.B.A.D. We discuss the physical phenomena.

M-VIII.2 11:45-12:15

FROM ELECTRICAL TO ALL OPTICAL IN-PLANE POLING OF POLYMER BASED ELECTROOPTIC MODULATOR, A. Donval*, E. Toussaere*, S. Brasselet**, J. Zyss*,**, *France Telecom-CNET/DTT/CDP/EQM, 196 Av Henri Ravera, 92225 Bagneux, France; **ENS Cachan, LPQM, 61 av. du Pres. Wilson, 94235 Cachan, France

Electrooptical polymer waveguide devices can be easily achieved by simple spin coating of polymer layers, with a transparent polymeric matrix as the passive buffer layer and with a side chain polymer as the active guiding layer. In order to create a noncentrosymmetric EO active material, a classical poling procedure may be adapted, whereby an electrical static field at elevated temperature, is applied over the side chain polymer resulting in the polar alignment of the chromophores parallel to the substrate. New poling procedures such as photo-assisted poling (PAP) as well as all optical poling can be used by direct illumination of the guiding active layer through the gap between coplanar electrodes. In PAP, the polar order is created by the static electric field acting on the molecules, whereas in all-optical poling the polar order is due to angular hole burning with a multipolar configuration reflecting the polarization symmetry of the interfering laser beams.

We report on a coplanar electrodes configuration phase modulator which is poled using those three poling procedures.

M-VIII.3 12:15-12:45

FILMS OF A NOVEL POLYDIACETYLENE FOR PHOTONIC STUDIES, A. Cravino, I. Moggio, C. Dell'Erba, D. Comoretto, C. Cuniberti, G. Dellepiane, DCCI, Via Dodecaneso 31, 16146 Genova, Italy; D. Grando and S. Sottini, IROE, Via Panciatichi 56, 50127 Firenze, Italy

We have prepared a novel polycarbazolyldiacetylene (PCDA) soluble in several organic solvents. The absorption spectra of PCDA are similar to those of other soluble polydiacetylenes with the exception of the benzene solution. In benzene the absorption spectrum of this polymer is characterized by a very strong and narrow excitonic peak followed by very weak resolved vibronic features and resembles the spectrum of a diacetylenic oligomer*. Upon increasing the temperature a chromatic reversible transition occurs, probably related to the disordering of the side groups, never observed before. Homogeneous films very promising for waveguiding as revealed by preliminary measurements have been prepared by the spin coating technique. Photobleaching effects will be discussed in terms of the modification induced by the radiation on the polymer.

*B. E. Kohler, D. E. Schilke, J. Chem. Phys. 86, 9 (1987)

12:45-14:00

LUNCH

Thursday, June 18, 1998

Jeudi 18 juin 1998

Afternoon

Après-midi

SESSION IX

Chairperson: Z. Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ, USA

- M-IX.1** 14:00-14:45 - Invited - **SPIN TRANSITION COMPOUNDS: FROM MOLECULAR MATERIALS TOWARD MEMORY DEVICES**, O. Kahn, Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS n°9048, 33608 Pessac, France
Some $3d^n$ ($4 \leq n \leq 7$) transition metal compounds exhibit a cooperative transition between a low-spin (LS) and a high-spin (HS) state. This transition is then abrupt and occurs with a thermal hysteresis, which confers a memory effect on the system. The inter-site interactions and thus the cooperativity are magnified in polymeric compounds such as $[\text{Fe}(\text{Rtrz})_3]_n \cdot n\text{H}_2\text{O}$ in which the Fe^{2+} ions are triply bridged by 4-R-substituted-1,2,4-triazole molecules. Moreover, in these compounds the spin transition is accompanied by a well pronounced change of color between violet in the LS state and white in the HS state. The transition temperatures of these materials can be fine tuned, using an approach based on the concept of molecular alloy. In particular, it is possible to design a compound for which room temperature falls in the middle of the thermal hysteresis loop. These materials have many potential applications, for example as temperature sensors, as active elements of various types of displays, and in information storage and retrieval.
- M-IX.2** 14:45-15:15 **TOWARDS HIGHLY EFFICIENT NONLINEAR OPTICAL CHROMOPHORES: MOLECULAR ENGINEERING OF OCTUPOLAR MOLECULES**, J-B. Baudin, R. Lorne, L. Jullien, M. Blanchard-Desce, Ecole Normale Supérieure, Département de Chimie (URA 1679), 24 Rue Lhomond, 75231 Paris Cedex 05, France and S. Brasselet, J. Zyss, Département d'Electronique Quantique et Moléculaire, France Télécom, 196 avenue Henri Ravera, 92225 Bagneux Cedex, France
"Octupolar" molecules are of particular interest in the field of nonlinear optics due to their potentially large quadratic nonlinearities.¹ In order to design molecules combining important quadratic hyperpolarizabilities and excellent transparency, we have implemented a strategy based on the design of organic chromophores of tetrahedral symmetry. By grafting of elongated conjugated rods on a central tetrahedral unit, large quadratic nonlinearities have been achieved while maintaining a wide transparency window in the visible range. Such optimized molecules are of particular interest for all-organic frequency doublers, if they can be incorporated in a polymer matrix allowing for "optical poling".²
¹ J. Zyss, Nonlinear Optics, 1991, 1. 3.
² C. Fiorini, F. Charra; J.-M. Nunzi, I.D. Samuel and J. Zyss, Opt. Lett., 1995, 20, 2469.
- M-IX.3** 15:15-15:45 **SUPPRESSION OF MULTIPHOTON FLUORESCENCE IN HYPER-RAYLEIGH SCATTERING**, G. Olbrechts, T. Munters, K. Clays and A. Persoons, Center for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium
Hyper-Rayleigh scattering has become widely accepted as a technique for the experimental determination of the first hyperpolarizability (second-order nonlinear polarizability) of molecules in solution. Multiphoton fluorescence can contribute to the incoherent scattering intensity, leading to an overestimation of this hyperpolarizability. A new technique is presented to eliminate this contribution from the hyper-Rayleigh scattering. High frequency modulation of the fundamental beam modulates both the immediate scattering and the time-delayed fluorescence. Due to the finite lifetime of the excited state leading to the emission, the fluorescence exhibits essentially complete demodulation (zero amplitude) while the scattering is unaffected. The high modulation frequency of the fundamental is obtained as a higher harmonic of the repetition frequency of a femtosecond pulse laser. The proper working of this approach is demonstrated with reference compounds. New results on fluorescing mono-, bi- and terchromophoric compounds will be presented.
- M-IX.4** 15:45-16:15 **POLYENOVANILLINS FOR NONLINEAR OPTICS**, T. Zabalun, T. Brotin, C. Andraud, A. Collet, Ecole Normale Supérieure de Lyon, 69364 Lyon Cedex 07, France and S. Brasselet, I. Ledoux, J. Zyss, Centre National d'Etude des Télécommunications, France-Télécom, Bagneux et LPQM, ENS-Cachan, France
The interest in nonlinear optics of polyenovanillins has been demonstrated for push-pull (with up to $n = 6$ double bonds), symmetrical donor-donor ($n \leq 11$) and octupolar systems. These polyenes were synthesized by using a straightforward Wittig-Horner polyvinylolation. The structures, conformations and spectroscopic properties of these polyenes were investigated by NMR, X-ray, electronic absorption and fluorescence spectroscopies; these properties, which are in good agreement with all-trans isomers were satisfactorily interpreted by molecular modeling and CNDO/S techniques. Large quadratic (up to $\beta^0_{\text{exp}} = 350 \times 10^{-30}$ esu for $n = 6$) and cubic (up to $\gamma_{1,34} = 11 \times 10^{-33}$ esu for $n = 11$) hyperpolarizabilities were obtained for longest polyenes with an exponential increase of the second-order with the conjugation length n . These data were explained in the light of CNDO/S calculations. Linear and nonlinear optical properties of octupolar systems were studied and compared to their rod counterparts; $|\beta|$ values were provided by HLS (harmonic light scattering) measurements as a function of the number of double bonds n .

16:15-16:45

BREAK

SESSION X

Chairperson: O. Kahn, Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, Pessac, France

- M-X.1** 16:45-17:30 - Invited - OPTICS AT NANOMETRIC SCALE: LOCAL PROBES AND ENHANCED FIELDS, L. Aigouy, J.C. Rivoal, S. Gresillon, A. Larech, H. Cory and **A.C. Boccara**, Ecole Supérieure de Physique et Chimie Industrielle de la Ville de Paris, UPR A0005 du CNRS, Laboratoire d'Optique Physique, 10 Rue Vauquelin, 75005 Paris, France
In the quickly growing field of near field microscopies (tunnelling, forces, optical...) we have developed a new approach which uses a metallic nanoantenna radiating the local field close to the sample surface towards a far field detector.
Such probe has demonstrated its ability of reveal local optical properties with a spatial resolution of 5nm in a broad spectral range (0.4 to 10µm).
We will show various kind of images revealing mainly optical contrasts in absence of topographical signals and discuss various domains of application of such approach, emphasising on enhanced local fields and studies of non linear effects.
- M-X.2** 17:30-18:15 - Invited - COMMUNICATION ON THE NANOSCALE THROUGH LOCALIZED ELECTRO-MAGNETIC RESONANCES ?, **V. Langlais**, R. Schlittler, J.K. Gimzewski, IBM Zürich Research Laboratory, Säumerstrasse 4, 8803 Rüschlikon, Switzerland
From the classical approach in microelectronic devices, the wires and interconnects in molecular nanoelectronics are based on physical entities as nanowires. Due to the size of these entities, the quantum mechanical principles steer the properties of such a connection. By using a Scanning Tunneling Microscope (STM), we have pioneered the realization of electrical contacts to single molecules and demonstrated the first single-molecule device capable of amplification. Nevertheless, the step to achieve actual devices through a fabrication scheme similar to microelectronic circuits has still to be cleared. Here, we propose an original approach which may be used to achieve communication on the nanoscale without any equivalent on the macroscopic scale due to the use of electromagnetic resonance modes. We have recently discovered that the electromagnetic characteristics of tunnel junction can be coupled to molecular systems. This concept requires specific molecular architectures. These designer molecules exhibit ultra high efficiency electroluminescence. The lateral extension of inelastic tunneling process being one order of magnitude smaller than the one of electromagnetic modes within the tunnel junction may be used to steer resonances on one or several molecules. We will present the results concerning a range of these designer molecules on various surfaces together with initial considerations of how they can communicate.
This worked has been partially supported by the European Union ESPRIT project "Nanowires" no. 23238 funded through the Swiss Federal Office for Research and Education.
- M-X.3** 18:15-18:45 NEAR-FIELD ELECTROLUMINESCENCE IN POLYMER LIGHT-EMITTING DIODES, F. Charra, S. Bouchel, O. Plessis, DRECAM-SRSIM CEA Saclay, 91191 Gif-sur-Yvette, France, and E. Gautier-Thianche, **J.M. Nunzi**, LETI (CEA - Technologies Avancées), DEIN/SPE, Groupe Composants Organiques, Saclay, 91191 Gif-sur-Yvette, France
Electroluminescence measurements on polymer Light-Emitting Diodes are usually performed on several mm² areas of layered structures. However, local characteristics of materials such as surface roughness, crystallinity, aggregation or defects may have dramatic influences on light-emission processes. We used the luminescence induced in a polymer LED by the biased tip of a Scanning Tunneling Microscope to study under air the local factors affecting polymer electroluminescence. We have observed the light emission induced by the scanned Platinum-Iridium tip of a STM in a 100nm-thick PVK film doped with a Coumarin dye, spin-coated on a transparent ITO electrode. The light is detected through ITO electrode by photon-counting and photon-maps are acquired simultaneously with STM images, in the Z (i.e. constant-current) mode. Two emission regimes are evidenced : the first emission observed when increasing tip bias occurs through discharges appearing as emission segments along the scan direction in photon maps. At higher voltages a regular emission regime is observed. These two regimes appear at different locations, that can be correlated to the characteristics surface profile measured simultaneously by STM.

POSTER SESSION

18:45-19:30 See programme of this poster session p. M-13 to M-18.

Friday, June 19, 1998

Vendredi 19 juin 1998

Morning

Matin

SESSION XI

M-XI.1 8:30-9:15 - Invited -

RELAXATION OF EXCITONS IN CONJUGATED POLYMERS, **M. Schott**, Groupe de Physique des Solides, UMR 75-88 du CNRS, Universités Paris 7 et 6, 2 Place Jussieu, 75251 Paris Cedex 05, France

Excitons play a key role in many electronic processes in undoped, semiconducting, conjugated polymers. They dominate the optical properties in absorption and in emission. They are neutral intermediate states in charge carrier recombination leading to electroluminescence. Conversely, interaction of excitons with other excitons, photons or impurity centres, is likely to play a part in photoconduction of conjugated polymers (such processes are well documented in conjugated organic molecular crystals). In all these cases, it is important to understand and quantify exciton relaxation processes, both radiative and non radiative.

In this talk, I shall first consider the importance of excitons in optical absorption. I shall then mostly discuss non radiative processes, and consider the role played by intrachain electron correlations and electron-phonon coupling -for instance the occurrence of self-trapping-, and by interchain interaction. The influence of gap states corresponding to excitons of Ag symmetry will be considered. Examples will be drawn from well-defined model systems such as polydiacetylene chains isolated in their crystalline monomer matrix, polyenes, or J-aggregates, and from technologically important materials such as PPV and substituted conjugated polymers.

M-XI.2 9:15-9:45

LUMINESCENCE OF OLIGOPHENYLENEVINYLENE FILMS DOPED WITH LOW-ENERGY GAP HOMOLOGUES, **D. Oelkrug**, **J. Gierschner**, **H.-J. Egelhaaf**, **U. Stalmach***, **K. Müllen****, Institute of Physical Chemistry, University of Tübingen, Germany ; *Dept. of Polymer Chemistry, Materials Science Centre, University of Groningen, The Netherlands, ** Max-Planck-Institut für Polymerforschung, Mainz, Germany

Phenylenevinylens are promising active materials for organic electroluminescent devices. However, the room temperature photoluminescence yields of films formed from unsubstituted oligo- (nPv) or polyphenylenevinylens (PPV) are only low ($\Phi < 0.1$) and strongly reduced against the yields of the film constituting molecules in dilute solution ($\Phi = 0.5 - 1$). Efficient quenching centers arise in the films from aggregates in close intermolecular side by side contact. Thus, Φ can be appreciably enhanced by modifying the molecular structures with distance keeping or contact angle changing substituents. In a different approach we raise Φ by incorporation of guest molecules with energy levels in between the HOMO-LUMO gap of the host. Typical guests are homo- logues (n + m)PV of the nPV host with m = 1,2,3,... additional conjugation units, or analogues from the series of conjugated oligothiophenes. The excited guest singlet states are efficiently populated in a consecutive reaction from the host and deactivate mainly by radiation so that the total luminescence yield at a guest mole fraction of $x = 5 \cdot 10^{-4}$ can exceed $\Phi = 0.6$. At low mole fractions of $x = 10^{-5}$ a competitive nonradiative host-guest charge separation process is operative which reduces Φ . However, this process is masked at higher x by the radiative channel. According to the rise and decay kinetics and the temperature dependences of guest and host luminescence efficiencies, a long lived intermediate must be populated from the primary excited excitons which is the source of the extreme long guest luminescence lifetimes in the order of 2 - 10 ns.

M-XI.3 9:45-10:15

MOMENTUM DEPENDENT ELECTRONIC EXCITATIONS IN OLIGOMERS: SEXIPHENYL AND SEXITHIOPHENE, **M. Knupfer**, **T. Pichler**, **M. S. Golden** and **J. Fink**, Institut für Festkörper- und Werkstofforschung Dresden, 01171 Dresden, Germany; **E. Zojer** and **G. Leising**, Institut für Festkörperforschung, TU Graz, Petersgasse 16, 8010 Graz, Austria; **M. Murgia**, **R. H. Michel**, **R. Zamboni**, **C. Taliani**, Istituto di Spettroscopia Molecolare, Consiglio Nazionale delle Ricerche, Via P. Gobetti 101, 40129 Bologna, Italy

We present momentum-dependent electron energy-loss measurements in transmission of the electronic excitations of sexiphenyl and sexithiophene in an energy range of 0 - 8 eV. These measurements allow one to study dipole allowed and forbidden singlet excitations which are polarized along the long axis of the molecules. The results of the two oligomers are very similar suggesting a universal behavior for such π conjugated systems. We show that our measurements can be used to obtain an estimate for the spatial extension of the final state wave function, i.e. the size of the electron-hole pairs created by the corresponding excitation.

10:15-10:45

BREAK

SESSION XII

Chairperson: **M. Schott**, Groupe de Physique des Solides, Univ. Paris 7 & 6, Paris France

M-XII.1 10:45-11:15

FIELD-ASSISTED FEMTOSECOND PUMP/PROBE MEASUREMENTS ON CONJUGATED SYSTEMS, **Ch. Zenz**, **G. Lanzani**, INFN, University of Sassari, Via Vienna 2, 07100 Sassari, Italy; **G. Cerullo**, **S. De Silvestri**, Politecnico di Milano, P.za Leonardo da Vinci 32, 20133 Milan, Italy; **W. Graupner**, **F. Meghdadi**, **G. Leising**, Inst. für Festkörperphysik, Petersgasse 16, 8010 Graz, Austria

We present field-assisted femtosecond pump-probe experiments in light emitting diodes of ladder-type poly(para-phenylene) (LPPP) and para-hexaphenylene (PHP). By modulation of the applied field we monitor directly the field-induced population of photo-generated species. The observed kinetics elucidate the mechanism of the charge carrier generation mechanisms in conjugated systems. The direct observation of the charge carrier generation in LPPP and its kinetics indicates a direct dissociation of singlet excitons into polarons. In PHP we observe a field-induced quenching of the singlet exciton leading to the formation of triplet excitons via an intermediate charged species.

SYMPOSIUM M

M-XII.2 11:15-11:45

CHARGE INJECTION AND TRAPPING EFFECTS IN DPOP-PPV POLYMER FILMS, F. Michelotti, V. Taggi, M. Bertolotti, Università degli Studi di Roma "La Sapienza" - Dipartimento di Energetica & INFM, Via A. Scarpa 16, 00161 Roma, Italy; and T. Gabler, H.H. Hörhold, Friedrich Schiller Universität, Jena, Germany; and A. Bräuer, Fraunhofer Institut, Jena, Germany

We report on the measurement of the Kerr electro-optic susceptibility in DPOP-poly-phenylene-vinylene films sandwiched between indium tin oxide and metal electrodes. Such polymer was designed and used for the application in third order non linear optical integrated devices.

The results, obtained by means of non linear reflectance ellipsometry, indicate the presence of charge injected and trapped in the polymer films under application of a dc voltage. The values of the Kerr $\chi^{(3)}$ susceptibility and of the total voltage drop on the film are evaluated. Time resolved measurements allow to investigate the process of charge ejection at several temperatures, giving information on the mobility of the carriers.

M-XII.3 11:45-12:15

EFFECT OF MOLECULAR ORDERING ON THE PHOTOPHYSICS OF ORGANIC HETEROMULTILAYER STRUCTURES, M. Muccini, E. Lunedei, P. Moretti, F. Biscarini, M. Murgia, R. Zamboni, and C. Taliani, ISM - CNR, Via Gobetti 101, 40129 Bologna, Italy; R.F. Mahrt, FB Physikalische Chemie der Philipps-Universität Marburg, Hans-Meerweinstrasse, 35032 Marburg, Germany

Conjugated polymers have among the largest optical nonlinearities and interesting charge generation and transport properties. The combination of both these characteristics is indeed appealing for optoelectronics. We report here on the spectroscopic characterisation of alternated multilayers of T_6 and C_{60} grown in UHV. First, we studied the influence of different film morphologies, induced by different growth conditions and thickness, on the optical properties of αT_6 thin films. In particular, we show the change in the spectral characteristics as the sample undergoes morphological transitions from dishomogeneous structure to grains and from grains to layer structure. Afterwards we have been able to identify the effect of the morphology of the constituting layers on the optical and electronic properties of the multilayer structure. The emission spectral features, the quantum efficiency of fluorescence and the temperature dependence of the fluorescence spectrum are consistent with the appearance of a new state due to the interaction of the different molecular layers.

M-XII.4 12:15-12:45

LIGHT EMISSION FROM WELL DEFINED MOLECULES, M. Hanack, M. Hohloch, D. Hohnholz, F. Lange, Inst. f. Org. Chemie LS II, Auf der Morgenstelle 18, 72076 Tübingen, Germany

We present a series of new, well defined, conjugated molecules and discuss their application as an emissive layer in organic light emitting diodes (OLEDs). Using molecules instead of conjugated polymers is of some advantage with regard to processability and spectroscopical characterisation. On the other hand, crystallisation of the molecules in some cases prevents the formation of a homogeneous layer. Thus, the molecules have to be tailored in order to reduce crystallisation tendency. Various molecules have been synthesised and their structure-property relationships have been examined. We describe the influences of side-chains, functional groups and molecular geometry on crystallisation tendency and fluorescence and electroluminescence emission maxima.

12:45-14:00

LUNCH

Friday, June 19, 1998

Vendredi 19 juin 1998

Afternoon

Après-midi

SESSION XIII

M-XIII.1 14:00-14:45 - Invited -

ORGANIC FIELD-EFFECT TRANSISTORS AND ALL-POLYMER INTEGRATED CIRCUITS, **M. Matters**, M.C.J.M. Vissenberg*, C.J. Drury, C. Mutsaers, C. Hart, P. Herwig and D.M. de Leeuw, Philips Research Labs, Prof. Holstlaan 4, 5656AA Eindhoven, The Netherlands, *also at Instituut-Lorentz, University of Leiden, The Netherlands

This presentation will summarize part of the progress made at Philips on (solution-processed) organic field-effect transistors. We derived an analytical expression to describe the temperature and gate-voltage dependence of the field-effect mobility in amorphous organic thin film transistors based on a percolation model of hopping between localized states. Furthermore, we have succeeded in making all-polymer transistors and integrated circuits. Fabrication technology and performance of these all-polymer IC's will be illustrated.

M-XIII.2 14:45-15:15

ORGANIC NONLINEAR OPTICAL THIN FILMS PREPARED BY MOLECULAR BEAM DEPOSITION AT OBLIQUE INCIDENCE, **B. Müller**, C. Cai, Y. Tao, A. Kündig, M. Bösch, C. Bosshard, P. Günter, Institute of Quantum Electronics, ETH Zürich, Switzerland

Organic thin films with second order nonlinear optical properties hold promise for applications in fast optical data processing. Their fabrication under well-defined ultra-high vacuum conditions, however, is difficult to achieve since the dipolar molecules have to be aligned noncentro-symmetrically. Using novel chromophores such as 4-[trans-2-(4-pyridyl-vinyl)]benzoic acid developed in our laboratory and which can be aligned in a head-to-tail fashion via strong H-bonds, we have realized the acentric ordering by molecular beam deposition at oblique incidence on glass, quartz, and sapphire under ultra-high vacuum conditions. Although this method is not yet optimized, second harmonic generation measurements clearly show the ordering of the organic molecules within the plane of incidence, resulting in a nonlinear optical coefficient comparable to that of Langmuir-Blodgett films (~1 pm/V). The average dipole of the organic film is found to be in-plane. The strong H-bonds between the molecules lead to a high melting point (350°C) and an excellent thermal stability of the organic thin films. The relation between the growth conditions and optical and morphological properties will be discussed in detail.

M-XIII.3 15:15-15:45

A COMBINED CAPACITY/IMPEDANCE AND PHOTOELECTRON SPECTROSCOPY INVESTIGATION ON THE METAL/ORGANIC INTERFACE IN LIGHT EMITTING DEVICES, **J. Laubender**, F. Baier, M. Solowski, E. Umbach, Universität Würzburg, EP II, Am Hubland, 97074 Würzburg, Germany

The charge transport and electroluminescence efficiencies in organic light emitting devices (OLEDs) are strongly influenced by the metal/organic interface, which is often described by the Schottky model. However, temperature-dependent current-voltage (IV) and capacitance-voltage (CV) measurements on sexithiophene-based OLEDs with different film thicknesses show deviations from this model, especially at low temperatures [1]. The frequency-dependent capacitance measurements reveal a strong contribution of the majority carriers to the current up to a frequency limit, which is characteristic for the organic layer. With decreasing temperature this frequency limit shifts by about one order of magnitude to lower values indicating a decreasing carrier mobility.

The results from CV spectroscopy are discussed in relation to results from photoelectron spectroscopy, which allow a direct determination of the "band-offsets" at the metal/organic and organic/ITO interfaces. These latter experiments were performed on metal contacts prepared under UHV and under a deliberate background pressure of O₂ or H₂O in order to model realistic device preparation conditions. The influence of chemical reactions at the interface due to chemical reactions on the band offsets will be discussed.

M-XIII.4 15:45-16:15

OPTICALLY DETECTED MAGNETIC RESONANCE STUDIES OF NANOSTRUCTURED PPV-COMPOSITES **E.J.W. List**, P. Markart, W. Graupner, G. Leising, Institut für Festkörperphysik, Technische Universität Graz Petersgasse 16, 8010 Graz, Austria; J. Partee, J. Shinar, Ames Laboratory-U.S. DOE, ISU, Ames, Iowa 50011, USA; R. Smith, D. Gin Dept. of Chemistry, Univ. of California, 94720 Berkeley, USA

We used the powerful experimental techniques of optically detected magnetic resonance to monitor the dynamics of singlet and triplet excitons as well as polarons of isolated poly(para-phenylenevinylene) (PPV) chains incorporated into a self-assembled matrix ordered at a nanometer scale and compare it with the results obtained for bulk PPV. The ordering is a result of the lyotropic liquid-crystalline character of the matrix material, which leads to the formation of a regular hexagonal array of channels with a diameter of about 1.5nm, in which the conjugated polymer molecules are contained.

END OF SYMPOSIUM M

SYMPOSIUM M

SYMPOSIUM M
POSTER SESSION

Thursday, June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-midi

Poster Session
18:45-19:30

- M/P1** FT-IR AND FT-RAMAN SPECTRA OF A SERIES OF OXIDIZED, α,α' DIETHYL END-CAPPED OLIGOTHIE-NYLS: A SPECTROSCOPIC STUDY OF CONJUGATIONAL MODEL DEFECTS, J. Casado, S. Hotta*, V. Hernandez and J.T. Lopez Navarrete; Departamento de Quimica Fisica, Universidad de Malaga, 29071 Malaga, Spain; *Matsushita Research Institute Tokyo, Inc. Advanced Material Research Laboratory, 3-10-1 Higashimita, Tamaku, Kawasaki 214, Japan
Conjugated conducting polymers and oligomers constitute a subject of research laying at the interface between solid-state physics and molecular science. In this field, Raman spectroscopy is a powerful tool for studying the structures of neutral and oxidized conjugated oligomers as finite models of polymeric materials.
In this work, chemically oxidized α,α' diethyl-protected thiophene-based oligomers ($n = 4, 5$ and 6) are investigated by FT-IR and FT-Raman spectroscopies in solid state. The chemical oxidation was carried out either with iodine vapour or nitrosyl salts to obtain the low and high oxidized species, respectively. The vibrational spectra of these compounds are compared with those obtained for neutral oligomers and polythiophene. These are used to characterize the molecular species associated to the conduction mechanism in oligomeric and polymeric systems derived from thiophene.
- M/P2** NONLINEAR OPTICAL PROPERTIES OF POLYMOLECULAR FILMS, V.A. Barachevsky, Photochemistry Center of Russian Academy of Sciences, 7a Novatorov Str., Moscow 117421, Russia
Advanced in the study of nonlinear optical properties for organic compounds in polymolecular layers which were prepared by the Langmuir-Blodgett (LB) technique are presented. Prominence is given to results of investigation of second (SHG) and third (THG) harmonic generation of laser radiation in connection with the development of integral optics. The dependencies between harmonic generation intensity and a compound structure, intermolecular interaction (aggregation, complex formation, etc.), surface pressure into a monolayer, a preparation procedure as well as composition of LB films are discussed. Particular attention is given to own results of the studying LB films based on different dyes. It was found that efficient SHG is manifested by H- aggregates of cyanine dyes and their complexes with metal ions containing in subphase. Composition of subphase determines the size of molecular domains for spiropyran compounds with negative photochromism. It was shown that this photochromic day is characterized by high SHG intensity. Formation of domains of big sizes may be prevented by use of copolymers with dye fragments. Lines of attack on the problem concerning the decrease of scattering of laser radiation in LB films are discussed too. In summary, photoinduced effects in LB layers of organic compounds are considered with the aim of photocontrol of nonlinear optical properties. The perspectives of investigations in this field are associated with making photocontrol reversible harmonic transformers of laser radiation.
- M/P3** THERMALLY AND OPTICALLY INDUCED SPIN TRANSITION EFFECT ON STRUCTURE OF IRON(II) POLYMERIC COMPLEXES BY XAFS SPECTROSCOPY, S.B Erenburg, N.V. Bausk, L.G. Lavrenova, Institute of Inorganic Chemistry RAS, 630090 Novosibirsk, Russia
Polynuclear iron(II) complexes of the composition FeL_3A_2 , where $\text{L} = 1,2,4\text{-triazole (trz)}, 4\text{-amino-}1,2,4\text{-triazole (atr)}, \text{A} = \text{Br}^-, \text{BF}_4^-, \text{NO}_3^-, \text{ClO}_4^-$ have been synthesized and characterized. The temperature of spin transition (T_c) varies over a wide range (175K - 400K) with the change of ligand or anion. The synthesized compounds can be used in perspective as materials for optical switches since their spin transition has a wide hysteresis loop and is accompanied by changes in color and in optical reflectance spectra.
Measurements of XAFS spectra were performed using synchrotron radiation of the VEPP-3 storage ring at the Institute of Nuclear Physics. In all studied polynuclear compounds the Fe-N and Fe-C interatomic distances increase upon the transition from the low spin (LS) to the high spin (HS) state by amounts from 0.12 to 0.24Å. The decrease of T_c appears to be associated with an increase in the Fe-N distances due to decreasing "electrostatic pressure" caused by the anion-cation interaction. Measurements of EXAFS and XANES spectra of the polynuclear spin-transition complexes FeL_3A_2 and $\text{Fe(atrz)}_3\text{SiF}_6$ at 4.2 K were performed without an optical treatment and after optical irradiation with a line 546 nm. The existence, at 4.2K, of long-lived optically excited metastable high-spin (LIESST) states was established for the $\text{Fe(atrz)}_3(\text{ClO}_4)_2$. The changes in structure upon the transition to a metastable HS state some differ from those in the thermally induced spin transition.
This work was supported by the Russian FBR (Pr. 96-03-32948).
- M/P4** STUDY THERMAL PROPERTIES OF ELECTRON IRRADIATED METALLIZED POLYIMIDE FILMS, A.I. Kupchishin, N.V. Slyunyaeva, K.B. Tlebaev, B.G. Tepikin, Almaty State University, Dostyk 13, 480100 Almaty, Kazakstan
The paper presents the results of experiments on temperature dependence of thermal conductivity and heat capacity of some metallized polyimide films irradiated with electrons of 2-6Mev. Accelerator ALU-6 was used to irradiate films with different integral dose (0-2 Gy). Cascade- probability model of generation of radiation defects in polymers (break of polymer chains) was developed. Such defects effect directly on the process of heat transport and heat capacity.
- M/P5** TWO PEAKS RESONANT MODEL OF ENERGY ABSORPTION BY IRRADIATED LINEAR POLYMERS, A.I. Kupcheshin, Almaty State University, Dostyk 13, 480100 Almaty, Kazakstan
Detailed experimental study showed resonant energy absorption at definite temperatures by some linear polymers (fluoroplast and others) on the background of monotone change in heat capacity $\lambda(T)$ and thermal conductivity $C(T)$. Curves of $\lambda(T)$ and $C(T)$ for fluoroplast exhibit two peaks in the room temperature region.
The paper presents two peaks resonant model of energy absorption. The first peak is associated with absorption of energy by oscillating system (models of string and spring) before the phase transition and the second one with energy absorption after the phase transition. Decrease of peak amplitude with increase of exposure dose is explained by destruction of material and shift of peak towards lower temperatures is due to decrease of effective length of elementary cell.

- M/P6** ION SHRINKAGE OF FLUORIDE POLYIMIDE, T. Trigaud, J.P. Moliton, M. Quillat, D. Chiron, UMOP, Faculté des Sciences, 123 Av Albert Thomas, 87060 Limoges, France
In the framework of the development of low cost optical devices for telecommunications, fluorinated polymers are very promising. The physical and chemical properties of polyimide derivatives make this polymer type the most suitable with silicon processes. Therefore, fluoride polyimide as 6FDA-ODA releases a good choice for etching of planar optical wave guides. Here is studied the shrinkage of 6FDA-ODA films after ion irradiation as a function of five parameters: the fluence, the fluence rate, the beam energy, the ion nature and the target temperature. In the [30-350]keV energy range for impinging ions, the shrinkage remains constant whatever the tested fluence rate is. A Saturation limit appears for fluence above 10^{16} ions/cm². The etching is linearly dependant on the ion beam energy and reaches a maximum for Na⁺ ions during irradiation carried out at high temperature.
- M/P7** FIELD-EFFECT ELECTROLUMINESCENCE IN A POLYMER CHANNEL, E. Gautier-Thianche, C. Sentein, A. Lorin and J.M. Nunzi, LETI (CEA - Technologies), DEIN / SPE, Groupe Composants Organiques, Saclay, 91191 Gif sur Yvette, France
We developed a new type of light-emitting device in which the emission layer is confined inside an Aluminium channel. A 1200Å Aluminium layer was first deposited on glass by vacuum evaporation and then carved using microlithography techniques. Channels were typically 1.5µm width. A 2000Å thick electroluminescent polymer film was spin coated on top of the Al-channel. The diode emits light under alternative voltages. It can be seen under room illumination. We studied the current-voltage characteristics and LED quantum efficiency. We also studied the effect of nitrogen gas on the emission spectrum. Efficient electroluminescence results from a field-induced ionisation and recombination process. No charge injection takes place at the electrodes in such device.
- M/P8** ORGANIC LIGHT-EMITTING DEVICES BASED ON OLIGO (PARA-PHENYLENE)S, D. Sainova, U. Scherf, V. Cimrova and D. Neher, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
Electroluminescent conjugated polymers have been intensively investigated in recent years with respect to their applicability as active materials in efficient light emitting diodes (LEDs). Polymeric LEDs consist of a thin layer of luminescent polymer between two metal electrodes. The performance of organic LEDs depends not only on the luminescence yield of the polymer but also on the balance of charge injection and transport processes in the layer. We have recently measured the emission zone of a single layer LED [1]. These experiments indicated that the quenching of excitons near the cathode as well as insufficient recombination might lower the overall device efficiency [2]. Therefore, the investigation of these mechanisms and their effect on device parameters is of significant importance.
We present a study of charge injection and transport in ladder-type oligo(paraphenylene)- LPPP - based blue light-emitting LEDs. In the case of organic LEDs two basic processes controlling the current - voltage performance are discussed: injection limited and space-charge limited currents. Varying the parameters of the devices - thickness of deposited polymer layer and the cathode material - these two limiting cases were observed in the device behavior. The transition between injection limited and space-charge limited current is investigated and discussed with respect to the performance and brightness of the LEDs.
- M/P9** ION BEAM ASSISTED ETCHING FOR THE REALIZATION OF OPTICAL GUIDES, B. Lucas, C. Moussant, A. Moliton, UMOP, Faculté des Sciences, 123 Av Albert Thomas, 87060 Limoges, France
Considering the easy implementation of polymers and of some of their electrooptical properties, a strong potential exists for their use as passive as well as active material in order to realize the interconnection of communication systems. The emergence of such systems is nevertheless conditioned by the performance that polymers must present and particularly the low guiding loss (0.3db/cm for rectilinear guides). The fluorinated polyimide (6FDA-ODA) from Du Pont's seems to be an excellent candidate for the realization of circuits for integrated optoelectronics. This realization will only be possible with the use of highly anisotropic etching techniques in order to obtain a good geometry of the guides. Etching by IBAE technique which uses a low energy ion (Ar⁺ or O⁺) beam to lead to a reactive flux, enables to combine the anisotropy properties of conventional ion etching (RIE) and to increase the etching rate. A study of the etching rate will then be led.
- M/P10** REALIZATION OF RED LIGHT-EMITTING DIODES WITH A CONFINEMENT LAYER, R. Antony, B. Ratier and A. Moliton, UMOP, Faculté des Sciences, 123 Av Albert Thomas, 87060 Limoges, France
In order to obtain a light emission with a red color, we have realized light-emitting diodes with an electroactive polymer: the poly(3-octylthiophene) or P3OT.
The internal quantum efficiency versus applied bias characteristic is very weak ($\eta_{int} = 0.03\%$). Thiophene are known to be electroactive material with a poor efficiency because there are lot of problems at the polymer-cathode interface.
In order to improve the electron injection, we have inserted a 2-(4-biphenyl)-5-(4-ten-butylphenyl)-1,3,4 oxadiazole (or butyl-PBD) layer between the polymer film and the calcium cathode. With this two-layers structure, we obtain a tenfold improvement in efficiency ($\eta_{int} = 0.25\%$).
We discuss the phenomenon.
- M/P11** REACTIVE ION BEAM ETCHING AND OPTICAL CHARACTERISATION OF POLYPARAXYLYLENE FILMS FOR WAVE GUIDE APPLICATIONS, B. Ratier, A. Moliton, UMOP, University of Limoges, 123 av Albert Thomas, 87060 Limoges, France, and P. Audebert, University of Franche Comté, Laboratoire de Chimie et d'Electrochimie Moléculaire, Route de Gray, La Bouloie, 25030 Besançon, France
Polyparaxylylene and polydichloroparaxylylene films have been deposited by vapour deposition polymerization on silicon substrates. Their good mechanical properties allows the preparation of self supported films for optical characterisation: UV-visible and IR absorption spectra present a good transparency of the material and the observation of interference fringes shows a good film depth reproducibility suitable for optical applications.
Reactive Ion Beam Etching (RIBE) with oxygene or argon ions of the films for ribbon wave guide fabrication will be compared with RIBE of fluorinated polyimide.
- M/P12** CHARACTERIZATION OF A POLYMERIC MULTILAYER STRUCTURE FOR ELECTRO-OPTIC APPLICATIONS BY MEANS OF THE ELLIPSOMETIC REFLECTION TECHNIQUE, V. Taggi, F. Michelotti, M. Bertolotti, Università degli Studi di Roma "La Sapienza" - Dipartimento di Energetica, Via Antonio Scarpa 16, 00161 Roma, Italy; and E. Toussaere, J. Zyss, France Telecom-CNET, Laboratoire de Bagneux, 196 Av. H. Ravera, 92225 Bagneux Cedex, France
The effectiveness of nonlinear organic polymers for fabricating photonics and electro-optics waveguiding devices has been well demonstrated. Among the main issues, the identification of a procedure for poling an electro-optic film when it is sandwiched between buffer layers, and the measurement of the induced electro-optic properties have gained importance nowadays.
We report on the measurement of the second-order properties of a poled nonlinear polymer film stacked between linear polymer layers, performed by using an ellipsometric reflection technique. The experimental set-up is described and measurements of the electro-optic coefficients for a multilayer structure at different wavelengths are shown. The technique allows to evaluate the ratio between the in-plane and normal-to-plane electro-optic tensor's components.

- M/P13** LASER INDUCED RELAXATION OF THE ELECTRO-OPTIC PROPERTIES OF POLED COPOLYMERS, F. Michelotti, G. Nicolao, V. Taggi, M. Bertolotti, Università degli Studi di Roma "La Sapienza"- Dipartimento di Energetica & INFM, Via A. Scarpa 16, 00161 Roma, Italy; and E. Toussaere, J. Zyss, France Telecom-CNET, Laboratoire de Bagneux, 196 Av. H. Ravera, 92225 Bagneux Cedex, France
We report on the measurement of the time relaxation of the electro-optic properties of poled side-chain copolymers under illumination with absorbed laser radiation. Films of side-chain Disperse Red1-PMMA were sandwiched between ITO and gold electrodes and poled with a standard temperature/electric field cycle. The decay of the electro-optic properties, measured by means of the Teng and Man ellipsometric reflection technique at $\lambda=830\text{nm}$, was measured for several intensities of a circularly polarised absorbed laser beam, $\lambda=514.5\text{nm}$, illuminating the sample. The relaxation shows a stretched exponential time dependence, with intensity dependent decay and stretching constants. The relaxation curves are compared with those obtained, for the same sample, in standard temperature stimulated non linear dielectric relaxation measurements.
- M/P14** STRUCTURAL CHARACTERIZATION OF TETRAHEXYLSEXITHIOPHENE ORDERED FILMS GROWN BY ORGANIC MOLECULAR BEAM DEPOSITION, C. Bota, S. Destri, W. Porzio, Istituto di Chimica delle Macromolecole del C.N.R., Via E. Bassini 15, 20133 Milano, Italy; A. Sassella, A. Borghesi, R. Tubino, Dipartimento di Scienza dei Materiali, Università di Milano, via Emanueli 15, 20126 Milano, Italy
The deposition of thin films of $3,3''4''''3''''''$ -tetrahexyl-2,2':5'',2'':5''',2''':5''''2''''''-sexithiophene (T6H4) has been performed in ultra-high vacuum conditions by using organic molecular beam deposition. Besides temperature and pressure, the substrate choice is the key factor in determining the properties of the deposited films.
From the structural analysis of samples deposited on different inorganic and organic substrates and the comparison with single crystals of T6H4 interesting information useful for the control of the structural order and the molecular orientation in the films are obtained. The different substrates considered are: amorphous silica, indium tin oxide, graphite, poly-tetrafluoroethylene, LB and self-assembled films, potassium phthalate, and mica. Epitaxy is observed on suitably oriented organic or inorganic single crystals, driven by their strong interaction with T6H4 molecules.
The results of structural investigations (XRD), compared with optical analyses (electronic absorption and PL), are presented and discussed in terms of both intermolecular and substrate-T6H4 interactions.
- M/P15** MODIFIED MELAMINE RESINS FOR OPTICAL APPLICATIONS, J. Mahler and G. Rafler, Fraunhofer Institute of Applied Polymer Research, Kantstrasse 55, 14513 Teltow, Germany
A new four-step synthetic route based on s-triazines like cyanuric chloride (2,4,6-trichloro-s-triazine) was developed to generate polymers for optical applications. In a first step the optical active component, a chromophore, was covalently bonded to the s-triazine- ring. In a second step the residual chlorides of the triazine was substituted by ammonia or primary amines. Then this functionalized melamine was treated with an aldehyde, generally formaldehyde, and subsequently alkylated with methyl or butyl alcohol. Further modification of the cyanuric chloride in the second step by diamines or dialcohols enables to lower the network-density and therefore increasing the elasticity of the resulting polymer. From solutions of the prepolymers thin films can be prepared by spin-coating or dipping. After heating these films for crosslinking the triazine-chromophores a melamine resin for optics and optoelectronics is formed.
By appropriate physical treatment these polymers can be used in second order nonlinear optics, optical data storage and other fields where polymers with chromophores find applications. The system combines nearly all properties requested by the telecommunication industry for optical devices: an enormous chemical and mechanical stability, high transparency and a very high concentration of optical active components. It is remarkable that the connected chromophores, e.g. azobenzenes, are stable till 350°C , the decomposition temperature of the melamine resins.
- M/P16** ELECTROPOLYMERIZATION OF OLIGOTHIOPHENE SELF- ASSEMBLED MONOLAYERS, A. Yassar, R. Michalitsch, C. Nougues, A. Morisset, C. Bournat, P. Lang, A. El Kasmi, Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry Dunant, 94320 Thiais, France
The chemical modification of surfaces with rationally designed microstructures is interesting for both fundamental and practical reasons. Molecular self-assembly is one of the simplest and most effective methods for the chemical modification of surfaces and gives a better control of structure at the molecular level. Self-assembled molecules and/or polymers have been used to build devices, to study the distance dependence of electron and energy transfer.
In this communication we report the synthesis and characterization of a series of oligothiophenes bearing n-alkylthiol at the α terminal position or β position.
All these monomers have been chemisorbed onto Pt and Au surfaces leading to self-assembled monolayer. The coverage level, molecular orientation of the molecules and electrochemical properties have been investigated.
The self-assembled monolayer formed from bithienyl and tertienyl bearing n-alkylthiol at the β position have been electropolymerized in the absence of the monomers in solution. The resulting self-assembled polymers show a better electroactivity than the polythiophenes.
- M/P17** SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF NOVEL ELECTRON TRANSPORTING MATERIALS: α , ω DICYANO OLIGOTHIOPHENES, A. Yassar, F. Demanze, C. Coupry* and D. Fichou, Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry Dunant, 94320 Thiais, France; *Laboratoire de Spectroscopie Infra-rouge et Raman CNRS, 2, rue Henry Dunant, 94320 Thiais, France
The design and synthesis of organic semiconductors are of current interest in view of their potential applications as active materials in a variety of electronic devices such as field-effect transistors and light emitting diodes. In the solid state, these organic compounds show a natural tendency for hole transport. This is typically the case for oligothiophenes whose p-type character has been evidenced in a variety of devices. One way to induce electron transport in these materials consists of increasing the electron affinity of the molecule by introducing electron-withdrawing substituents on its conjugated backbone. With this aim, we have synthesized a series cyano oligothiophenes. In this communication we describe the synthesis of these compounds as well as their optical, electrical and X-ray characterization.
X-ray investigation of cyano-substituted oligothiophenes reveals many structural similarities. For example, all these molecules adopt a π -stack structure with a small interplanar staking distance. We note that such an arrangement is in contrast to the usual herringbone structure observed for non-substituted oligothiophenes.
The UV-visible absorption spectra of thin films show a bathochromic shift as compared to solutions spectra, with two narrow peaks located at low energy. This unusual behavior can be interpreted in terms of charge transfer excitons which are commonly observed in molecular semiconductors.
The I-V characteristics of $M_1/6T(CN)_2/M_1$ sandwich structures have been analyzed in order to obtain information on the transport properties of the cyano-substituted oligomer. $Au/6T(CN)_2/Au$ structures show symmetric I/V curves with low current densities. The low hole injection rate at Au electrodes can be ascribed to a large energy barrier. By contrast, the use of low work function metals such as Ag and Al allows high current densities to flow through the device, thus providing evidence for efficient electron injection and transport.
- M/P18** AUTOMATION OF SCIENTIFIC RESEARCH, SCIENTIFIC RESEARCH AND RADIATION TREATMENT OF LARGE VOLUME OF PRODUCTS WITH COMPLEX OF ACCELERATORS OF ALMATY STATE UNIVERSITY, E.K. Balafanov, NA. Voronova, L.G. Kolodin, A.I. Kupchishin, B.A. Tronin, V.V. Fomintsev, Almaty State University, Dostyk 13, 480100 Almaty, Kazakstan
Complex of two accelerators have been established in Almaty State University. It is designed for scientific research, experimental and technological operations and radiation treatment of large volume of production. Experimental complex consists of electron accelerator ALU-6 comprising changeable wave guide (energy 2-6 Mev, beam current up to $1500\text{ }\mu\text{A}$) and ion accelerator of Vezuvii type (energy up to 100 kev and beam current up to $1000\text{ }\mu\text{A}$), laboratory setups and two processing lines for treatment of large and mean volumes of products. Such operations were authorized. Complex was used for electron beam sterilization of some batches of one piece syringes (2 and 5cm^2) of Luer-2 and Luer-5 type. Ion implantation of nitrogen in Ti and W was carried out to harden surface of material.

- M/P19** A NEW METHOD TO EVALUATE THE BENDS IN POLYMER OPTICAL FIBRES, M. Machhout*, R. Attia and A. Bouallègue, Laboratoire des Systèmes de Télécommunications, Ecole Nationale d'Ingénieurs de Tunis, BP37, Le Belvédère, 1002 Tunis, Tunisia; *Faculté des Sciences de Monastir, 5000 Monastir, Tunisie
When light propagates along a polymer optical fibre that bends sharply, an important amount of power can be lost through radiation around the bend. In this paper, the power distribution in the core of a bend multimode step index fibre is determined on the basis of ray tracing method as a function of the angle round the bend, and as a function of the bend radius of curvature. Different bend shapes can cause very different radiation losses around the bend. The purpose of this paper is to show which curves give rise to the lowest attenuation and identify the reasons. The curved optical fibre is considered as a torus which parametric equations depend on the angle and on the radius of curvature. The intersection of a luminous ray propagating inside the straight fibre with the interface core-clad is determined by equalising equations of propagation. With those of the torus. The solution is obtained numerically. The direction of the reflected ray is then determined in a local frame (frame of Frenet). Knowing the new co-ordinates of the luminous ray, one can follow its evolution inside the curved fibre. At each reflection, the power of the ray is lessened by a certain quantity given by Fresnel relations. At the exit face, one establishes the distribution of the light and its attenuation for different rays and angle of curvature.
The influence of the bend shapes on the total radiation loss for two types of the most common optical fibres has been analysed. A circular shape causes slightly higher attenuation than an elliptical shape. Nevertheless, curves with sharp sections are always bad.
- M/P20** POLYMER-C60 EXCITON MIXING, S.V. Rotkin, Ioffe PTI, Polytechnicheskaya 26, 194021 St-Petersburg, Russia
The recent progress in the photovoltaic device fabrication on the base of fullerene-polymer composites reflects the interesting conducting and photo-conducting properties of the composite material. A particular interest to the charge transfer processes (e.g. exciton decay/recombination) from one component to other is in the focus of various application (see [1]). The semiconducting nature of the single fullerene cluster being the natural zero-dimensional quantum dot object allows to treat its excitations basing on early Frenkel ideas [2] of the small radius exciton. The same time a polymer excitation seems to be rather delocalized along the chain and does not look easy to mix with C60 exciton.
We propose a simple Huckel-like model to calculate the PPV excited states as well as C60 ones in a general approach. The symmetry analysis shows that the localized exciton modes exist in the polymer chain. Though additional symmetry occurs at zero k, the excitation wavenumber, which leads to additional transitions, it breaks with $k > 0$. The mixing of the local mode with the proper fullerene exciton is further discussed.
The fullerene dipole-active (singlet) and non-active (triplet) exciton were simulated within the TBA dipole-dipole interaction model in the nearest neighbour approximation as well as in full 60 atom lattice accounted. The group theoretical approach allows the analytical derivation of all eigenspectrum in the former case.
[1] A.A.Zakhidov et.al. Synt.Met.77, 127 (96)
[2] J.I.Frenkel, Phys.Rev.37, 17; ibid, 1276 (31)
- M/P21** LIGHT SCATTERING INSIDE POLYMER OPTICAL FIBERS, S. Jarboui, M. Machhout, L.S.Télécoms, Ecole Nationale des Ingénieurs de Tunis, BP37, Le Belvédère, 1002 Tunis, Tunisia
We are studying the light scattering effect on the light power distribution in polymer optical fibers (POF) on the basis of an improved statistical light ray (LR) theory. The LR is defined as a physical entity having a given state (direction). The exciting field scalar function is assumed to be the probability amplitude for finding a LR into the POF entrance face. Monte Carlo method is used to achieve LR random drawings. The scattering particle cross section position is randomly drawn from a Poisson process. At the drawn cross section, we proceed by a second random trial to locate the scattering particle position conformably to a Rayleigh process. If the light ray is touching the scattering particle, the scattered light ray direction is deduced from the incident one by a spatial rotation with random Euler angles and random phase variation. A constant rectangular window is opened at random positions of outlet face to determine the field pattern resulting from interference of the set of LR reaching the POF end. The method was used to study natural steady state power distribution in a straight POF.
- M/P22** ORIENTATIONAL DYNAMICS OF DOPING CHROMOPHORES IN LOW T_g PHOTOREFRACTIVE POLYMERS, J. Muller, C. Melzer, O. Cregut, A. Fort, L. Mager, J.-F. Nicoud*, S. Méry*, GONLO, GMO*, IPCMS, 23, rue du Loess, 67037 Strasbourg Cedex, France
It has been demonstrated that the high photorefractive performances of low T_g polymers doped with push-pull molecules are connected to the ability of the chromophores to rotate in the material. We have studied this process in carbazole functionalized polysiloxane doped with chalcone derivatives. We have characterized the relevant molecular properties of different chalcones molecules dilute in a solvent, such as dipolar moment, molecular birefringence and quadratic hyperpolarizability. These parameters have been compared to the values deduced from Maker fringes and ellipsometric measurements performed on 100 micron thick samples constituted by chalcone doped polymers. Our results point out that the orientation of the molecules, connected with the dynamics of both second harmonic generation and refractive index variation, depends on the nature of the doping molecules and on the history of the samples. These results help in the understanding of significant mechanisms which govern efficient photorefractive effects.
- M/P23** RAMAN SCATTERING OF LOW-DEFECT POLYACETYLENE, V.M. Kobryanskii, Institute of Chemical Physics, Kosygin St. 4, 117977 Moscow, Russia, D.Yu. Parashuk, Moscow State University, Moscow, Russia, A.N. Shegolikhin, Institute of Biochemical Physics, Moscow, Russia, A.H. Kuptsov, Federal Center of Forensic Science, Moscow, Russia, N.N. Melnik, P.N.Lebedev Physical Institute, Moscow, Russia
A new class of acetylene polymerization catalysts - binuclear compounds of Re - and a method of low-defect polyacetylene (PA) compositions synthesis were discovered. Compositions: - can be prepared in the form of solutions, films and plates; - have high stability; - are characterized by the pass-band in the region of 0.75-2.5 μm ; - are characterized by extremely high intensity of Stokes and anti-Stokes Raman scattering for resonant and non-resonant conditions.
The PA Raman cross-section was evaluated for a PA-polyvinylbutyral (PVB) solution in n-butanol. For excitation by a ND:YAG laser at 1064 nm the intensities of n-butanol bands in the interval from 1000 cm^{-1} to 1500 cm^{-1} were comparable to those of PA dissolved, in spite of the very high dilution ($10^{-8} \text{ g cm}^{-3}$). For PA-PVB films and plates the intensities of PA vibrations at $\sim 1070 \text{ cm}^{-1}$ and $\sim 1460 \text{ cm}^{-1}$ for non-resonant and resonant anti-Stokes Raman scattering were much more intensive than it follows from Boltzman distribution function.
PA compositions could be used as material for non-linear optical devices, Raman lasers, security of objects and documents against forgery and as a standard for Raman spectroscopy.
- M/P24** PHOTO- AND ELECTROLUMINESCENCE OF DOPED POLYMERS IN LANGMUIR-BLODGETT STRUCTURES, A.A. Avdienko, Institute for Low Temperature Physics & Engineering, NAS of Ukraine, 47 Lenin Ave., 310164 Kharkov, Ukraine, B.M. Krasovitskii, O.V. Tolmachov, K.B. Volodarskii, N.I. Voronkina, Institute for Single Crystals, NAS of Ukraine, 60 Lenin Ave., 310001 Kharkov, Ukraine
In this paper we report photophysical properties of organic polymer light emitting diodes (LED's) which were prepared both by Langmuir-Blodgett (LB) technique and by spin-coating. We fabricated electroluminescent cells using $\text{In}_2\text{O}_3/\text{SnO}_2$ transparent conducting electrode, N-polyvinylcarbazole films doped with tetraphenylbutadiene (TPB) (3 molar percents), polymethylmethacrylate (PMMA) films doped with 2-(4-biphenyl)-5(4-pentaphenyl)-1,3,4-oxadiazole (PBD) (in ratio 1:3) and metallic electrode Mg:Ag. The profiles of electroluminescence (EL) spectra of LED's fabricated by spin-coating are practically identical to photoluminescence (PL) spectra of these LED's. These spectra have characteristic peak at 2.82 eV as in PBD PL spectrum. EL spectra of multilayer LB structures have four characteristic peaks at 3.1, 2.54, 2.21 and 1.91 eV. We performed deconvolution of the EL spectra by using Gaussian lineshapes for each of one of the four emission bands. The EL spectra differ essentially from the PL spectra of these LED's and LED's fabricated by spin-coating. For evaluating of nature of above EL spectral properties we studied PL spectra and excitation PL spectra for TPB and PBD in solutions, polymers and powders. We studied also influence of number of layers on PL and EL profiles for LB LED's. We concluded that boundary effects explain some peculiarities of these spectra. We discuss possible nature of EL centers.

- M/P25** LUMINESCENCE OF C_{60} THIN FILMS AT LOW TEMPERATURES, A.A. Avdienko, V.V. Eremenko, N.B. Silaeva, Yu.A. Tiunov, P.V. Zinoviev, Institute for Low Temperature Physics and Engineering, National Academy of Sciences, Kharkov 310164, Ukraine, N.P. Churakova, N.I. Gorbenko, and A.T. Pugachov, Kharkov State Polytechnical University, 310002 Kharkov, Ukraine

We present results on fullerite C_{60} low temperature photoluminescence (PL) using C_{60} thin films. For the first time the PL spectra of the free single crystal films were studied. The C_{60} films were deposited onto NaCl wafer using 10^{-3} Pa vacuum by 99.9 % pure material to obtain a typical film thickness of 10 ± 0.1 nm. The free C_{60} films prepared by dissolving substrate in water were located on a copper net. The film structure was analyzed by standard electron diffraction techniques. The structure analysis showed that the films are homogeneous and (111)-oriented crystalline ones. The amorphous or nanocrystalline nonoriented films were prepared due to selection of a deposition rate, substrate temperature, and film thickness. The PL spectra of C_{60} thin films were measured at 5 K covering spectral range from 1.5 to 1.85 eV. The C_{60} PL spectra both for the free crystalline thin films and crystalline thin films on NaCl substrate are similar with broad peaks at 1.78, 1.71, 1.6, and 1.52 eV. This similarity means that NaCl substrate weakly influenced on fullerite C_{60} excited states. The PL spectra overall profile and peak position don't change depending on the excitation energy. We attribute the PL band at 1.71 eV to radiative recombination of a self-trapped exciton of an excimer type without inversion center. We attribute the PL band at 1.78 eV to radiative recombination of X-traps on crystalline surfaces. The strong decrease of the intensity of the 1.78 eV peak in PL spectrum of the amorphous or nanocrystalline thin films supports the proposed hypothesis.

- M/P26** THEORETICAL INVESTIGATION OF PHENYLENE-BASED MATERIALS IN THEIR PRISTINE AND DOPED STATE, E. Zojer, Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria; J. Cornil and J.-L. Brédas, Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, 7000 Mons, Belgium; G. Leising, Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria

Phenylene-based organic materials play an important role in organic device technology especially in light emitting diodes and displays. We have investigated their geometry and optical transitions in both pristine and doped states, paying special attention to chain-length effects and the implications of inter-ring twists (also considering bridged ladder type molecules). The geometries for the pristine and doped chains are optimized using the AM1 method including configuration interaction for excited states. Optical transitions are calculated in the framework of the INDO approach coupled to a single configuration interaction technique to include electron-electron correlation effects. Our calculations give an extent of four benzene rings for the geometry modifications associated with the formation of polarons and of six rings for the bipolarons (without explicit account of counter-ions). We predict two sub-gap absorption features for polarons in short-chain molecules and a single peak for bipolarons. In longer chains and for interacting bipolarons, this situation changes considerably within the used theoretical framework. It is also shown that inter-ring twist angles do only play a significant role in the absorption spectrum of undoped molecules.

- M/P27** SYNTHESIS AND PROPERTIES OF POLY(ARYLENE VINYLENE)S WITH CONTROLLED STRUCTURES, Ch. Lartigau, W.J. Feast, Durham University, South Road, Durham DH1 3LE, UK and F.C. Cacialli, R.H. Friend, Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 0HE, UK

Poly(arylene vinylene)s have attracted interest as the light emitting layer in LEDs. Such polymers may be made by several ways. We have used McMurtry, Yamamoto and Suzuki methodologies to make different poly(arylene vinylene)s. We synthesised polymers with meta linkages between phenylene and vinylene groups in an attempt to increase the energy gap and to shift the light emitting wavelength towards the blue region. The number and geometrical connectivities of the phenylenes constituting the arylene portion of the repeat unit, the cis/trans distribution have been varied in a controlled way. Relatively high molecular weight distributions were produced by fractionation. Results correlating the details of polymer structure with the observed photoluminescence will be discussed along with some early results on electroluminescence, and compared with some previous results on other poly(arylene vinylene)s.

- M/P28** MOLECULAR-DOPED POLYMERIC LANGMUIR - BLODGETT FILMS FOR MOLECULAR ELECTRONICS, N.I. Voronkina, K.B. Vodolazhsky, A.V. Tolmachev, Institute for Single Crystals, Lenin Ave., 60, 310001 Kharkov, Ukraine

Stable LB films of polymethylmetacrylate (PMMA) and poly - N - vinylcarbazol (PVK) doped by amphiphilic and non - amphiphilic organic luminophors have been prepared on aqueous surface and in multilayered structures on ITO substrate. Concentration dependences of photoluminescence have been studied for PMMA LB films doped by 2-(4-biphenyl)-5-phenyl-oxadiazole-1,3,4 derivatives containing alkyl substituents $N_{17}I_{35}$, $N_{51}I_{11}$, $(N_{13})_3$, $[Ph-(CH_2)_3]_2$ within dopant concentration range from 0 to 75 mol.%. Concentration limits have been found for the luminophor distribution and for the crystalline phase formation in the polymer monolayer depending on the luminophor molecular structure that defines the molecular orientation on water surface in the stretched liquid phase state. The probability of eximers and fluorescing ordered aggregates formation in the solid crystalline phase has been also estimated. Such LB films have been found to be effective electron transporting layers and were used to produce multilayer LEDs having stable operating characteristics in room environment. To this end, the LB films were used in combination with those of tetraphenyl-butadiene doped PVK as the hole-transporting layer.

- M/P29** EFFICIENT SINGLE LAYER YELLOWISH LIGHT EMITTING DIODES MADE OF A BLEND OF A LADDER-TYPE POLY(P-PHENYLENE) AND POLYTHIOPHENE E.J.W. List, L. Holzer, S. Tasch, G. Leising, Institut für Festkörperphysik, Technische Universität Graz Petersgasse 16, 8010 Graz, Austria; S. Luzzati, Istituto di Chimica delle Macromolecole-CNR, Via Bassini 15, 20133 Milano, Italy

We present the realisation of efficient yellow polymer light emitting diodes (PLEDs), in a simple single layer configuration, which is of considerable interest because of the ease of the production of the PLEDs. We found that the electroluminescence-quantum-efficiency of PLEDs made of a blend of a blue emitting ladder-type poly(p-phenylene)(m-LPPP) and small amounts of a red emitting poly(thiophene) (PT) is significantly improved compared with PLEDs fabricated of pure m-LPPP. In this paper we compare the photoluminescence and electroluminescence efficiencies as well as the I/V characteristics of PLEDs made of different concentrations and discuss the observed aggregation effect of PT in the blend, which strongly alters the photophysical properties.

- M/P30** TOWARDS THE 3D SOLID PHOTONIC CRYSTALS, N. V. Gaponenko, V.V. Shushunova, Belarusian State University of Informatics and Radioelectronics, 220027 Minsk, Belarus, A.M. Kapitonov, D.A. Yarotsky, S.V. Gaponenko, Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, 220072 Minsk, Belarus, V.N. Bogomolov, Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia and J. F. McGilp, Trinity College, Dublin 2, Ireland

We have synthesized a novel solid composite material exhibiting a photonic band gap in the visible range. The material consists of monodisperse SiO_2 globules arranged in a close-packed f.c.c. lattice. The periodical sublattice of voids of the samples was filled with sol-gel derived TiO_2 or Fe_2O_3 films with the refractive index in the range 2.3-2.4. The samples exhibit a photonic stop band in visible range, which manifests itself as a dip in the optical transmission spectrum or as a peak in the light reflection spectrum. Influence of photonic band gap on spontaneous emission of Tb^{3+} and Eu^{3+} ions embedded into this 3D dielectric lattice is in progress.

- M/P31** AN ORGANO-MINERAL CRYSTAL FOR BLUE SHG: CRYSTAL GROWTH AND QUADRATIC OPTICAL EFFECT OF 2A5NPCL, N. Horiuchi, F. Lefaucheux, LMCP, Univ. Paris 6 et 7, Paris, A. Ibanez, CNRS, Grenoble and D. Josse, J. Zyss, CNET/DTT, Bagneux, France
Due to the high occupancy of the chromophore in unit cell ($\bullet 184\text{\AA}^3/\text{molecule}$), the crystal of 2-amino-5-nitropyridinium chloride (2A5NPCL) is expected to exhibit a large quadratic optical effect.
The crystal is grown by temperature decrease in different ways; (1) at low supersaturation rate ($<1\%$) in a convective medium (solution) (2) with a small mass transfer in a diffusive medium (gel). In both methods, the crystalline quality examined by X-ray topography is rather good.
Using the coefficient d_{24} of KTP as reference, two effective coefficients of 2A5NPCL for SHG are determined as $1.9d_{24}$ for type I and $3.6d_{24}$ for type II at $1.32\mu\text{m}$. From these results, three of four independent coefficients (d_{12} , d_{13} and d_{14}) are deduced. Since the range of transparency is from 410nm to 2000nm , the SHG at 450nm is also demonstrated. Preliminary results lead to an efficiency of 2% (type I) for a fundamental energy of 2mJ and a pulse duration of 7ns .
- M/P32** LINEAR AND NON-LINEAR GRATINGS IN DR1 SIDE CHAIN POLYMERS, P. Labbé, E. Toussaere, France Telecom-CNET/DTT, BP 107, 196 Av Henri Ravera, 92225 Bagneux Cedex, France
Linear (refractive index) and non-linear (second order non linear optical susceptibility) gratings are of primary interest in optoelectronics. While linear gratings may be used for filtering or wavelength selective coupling, non linear gratings may find applications in active devices such as second harmonic generators, parametric generators or all optical switches through cascading of second order susceptibilities.
We report on a simple method for the inscription of linear or non linear gratings in DR1 side chain polymer thin films or waveguides. The technique is based on the photoisomerisation induced reorientation properties of such a material under irradiation with an Argon ion laser. It avoids the use of interdigitated electrodes for the selective orientation of the dyes, can be easily applied to a waveguide geometry and results into a good orientational stability. Sample characterization involves polarized microscopy and second harmonic generation.
- M/P33** ERBIUM PHOTOLUMINESCENCE IN SOL-GEL DERIVED TITANIUM DIOXIDE FILMS, N. V. Gaponenko, A. V. Mudryi, O. V. Sergeev, V. E. Borisenko, Belarusian State University of Informatics and Radioelectronics, P. Browki 6, 220027 Minsk, Belarus, H. Gnaser, Institut für Oberflächen- und Schichtanalytik, Universität Kaiserslautern, 67663 Kaiserslautern, Germany.
Titanium dioxide films are commonly considered as a perspective application for active planar waveguides because of a high value of refractive index ($2.3 - 2.4$). In this communication we investigated erbium photoluminescence in titanium dioxide film fabricated by sol-gel method from a $\text{Ti}(\text{OC}_2\text{H}_5)_4$ precursor. The titanium dioxide films were built up layer-by-layer by a spin-on technique on sublayer of porous anodic alumina $2.2\mu\text{m}$ in thickness fabricated on silicon substrate. The procedure of filling the pores by sol-gel derived composition, the concentration of the elements and their depth distribution in porous anodic alumina were investigated by the means of SIMS-analyses. Room temperature photoluminescence at $1.53\mu\text{m}$ which we associate with $^4I_{13/2} - ^4I_{15/2}$ transitions of Er^{3+} ions is observed from spin-on film after deposition of the first layer. Its intensity increases by one order of magnitude for ten repeated depositions of spin-on films. Comparison of SIMS-data obtained after deposition of the first and the tenth layer shows that the pores of anodic alumina were filled with luminescing material completely and result in an increase of the Ti and Er concentration to 10^{-1} and $4 \cdot 10^{-2}\%$, respectively, and the formation of a thin layer enriched in Ti, O and Er on top of the porous Al_2O_3 .
- M/P34** APPLICATION OF HIGH RESOLUTION SCANNING PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE TO ASSESS THE LATERAL HOMOGENEITY OF ORGANIC LEDs AND PLANAR MICROCAVITIES, L. Berthelot, M. Garrigues, J. Tardy, J. Joseph and B. Masenelli, LEAME (UMT CNRS 5512), Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France
Scanning photoluminescence (SPL) is now a well known and widely used method for characterizing the electronic properties of semiconductor surfaces. Lateral homogeneity of wafers and epilayers can thus be investigated with quite a high lateral and spectral resolution. This analytical method, originally developed in our laboratory for III-V semiconductors, was adapted for thin films of organic materials, organic LEDs and planar organic microcavities.
The SPL method used here consists in focusing filtered light from a W-lamp with a microscope objective onto the sample, collecting through the same objective the emitted photoluminescence and analysing it with conventional monochromator and detector. The lateral resolution is about $40\mu\text{m}$. This method was used to investigate the influence of the concentration and of the nature of the host polymer (PVK or PMMA) on the distribution of dyes or of small luminescent molecules dispersed in these two matrices. Results are also presented showing the influence of lateral homogeneity of dielectric Bragg mirrors on the emission spectra of planar microcavities. Finally, electroluminescence instead of photoluminescence imaging can be carried out. This method, called Scanning ElectroLuminescence Imaging Microscopy (SELIM) is shown to provide further insight on the organic LEDs characterization.
- M/P35** TOWARDS HIGHLY EFFICIENT NONLINEAR OPTICAL CHROMOPHORES: MOLECULAR ENGINEERING OF CHARGED PUSH-PULL MOLECULES, V. Alain, M. Blanchard-Desce, Ecole Normale Supérieure, Département de Chimie (URA 1679), 24 rue Lhomond, 75231 Paris Cedex 05, France and S. Brasselet, I. Ledoux, J. Zyss, Département d'Electronique Quantique et Moléculaire, France Télécom, 196 avenue Henri Ravera, 92225 Bagneux Cedex, France
The elaboration of nonlinear optical (NLO) materials has attracted considerable interest for the past two decades due to potential applications in telecommunications, optical data storage and optical information processing. In particular, organic materials, that allow for both molecular and supramolecular engineering of molecular and macroscopic nonlinearities are of particular interest. Within this framework, we have investigated an approach based on the optimization of so-called push-pull molecules¹. By playing on both the charge and aromaticity of the end groups, chromophores displaying huge quadratic (β) and cubic (γ) hyperpolarizabilities have been obtained. Issues related to application to in-situ and real-time monitoring of electric potentials in biological media will be discussed.
¹ M. Blanchard-Desce, V. Alain, P.V. Bedworth, S.R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus and R. Wortmann; Chem. Eur. J., 1997, 3, 1091.
- M/P36** OPTICAL CONSTANTS OF HIGHLY ORIENTED OLIGOTHIOPHENE FILMS AND NANOPARTICLES, H.J. Egelhaaf, J. Haiber, J. Gierschner, D. Oelkrug, Institute for Physical Chemistry, University, Auf der Morgenstelle 8, 72076 Tübingen, Germany.
For both, the effective design and the theoretical understanding of organic thin film devices the optical constants of the films must be known. We have determined the optical constants of vapor-deposited oligothiophene films in the wavelength range from 240nm to 800nm by measuring their angular resolved polarized transmission and reflection spectra and fitting the data to the Fresnel equations for uniaxial systems. In the region of the main absorption band the absorption coefficient normal to the surface reaches $k_n \approx 1$, whereas hardly any absorption is found for the direction parallel to the surface. The component of the refractive index along the surface normal varies between $n_n \geq 3$ on the low energy absorption edge and $n_n \leq 0.6$ on the high energy side of the absorption band, while the component parallel to the surface shows only little dispersion. This anisotropy causes a blue-shift of the absorption maximum against solution by several thousands of wavenumbers. Very similar optical constants are found for colloidal oligothiophene nanoparticles by fitting the results of light scattering experiments to Mie-theory of anisotropic particles. The optical constants of films and nanoparticles can only be rationalized by assuming at least two electronic transitions in the region of the main absorption band, which is supported by fluorescence anisotropy data.

E-MRS'98 SPRING MEETING



SYMPOSIUM N

Materials and Processes for Submicron Technologies

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SYMPOSIUM N

Tuesday, June 16, 1998

Mardi 16 juin 1998

Afternoon

Après-midi

SESSION I - Metallizations, Part 1

- N-I.1** 14:00-14:45 - Invited - INTERCONNECT TRENDS IN MICROELECTRONICS, **E. Martinez-Gutiérrez**, Bell Labs, Murray Hill, Lucent Technologies, New York, USA
- N-I.2** 14:45-15:00 THE DEPENDENCE OF THE NUCLEATION AND GROWTH OF CVD Al FILM ON THE TiN LINER DEPOSITION METHOD, **M. Avinun**, W.D. Kaplan, M. Eizenberg, Department of Materials Engineering, Technion, Haifa, Israel, T. Guo and R. Mosely, Applied Materials, Santa Clara, CA, USA
CVD Al followed by "warm" PVD Al(Cu) on top of a TiN/Ti liner is a very promising approach for filling high aspect ratio vias. To avoid oxidation this sequence of processes must be carried out without air exposure. In this work we have investigated the nucleation and growth of CVD Al on a TiN liner where the depositions were carried out in an integrated cluster tool (Endura™). A number of methods for deposition of the TiN were compared, such as PVD and MOCVD followed by H₂/N₂ plasma treatment. For each type of TiN, Al films were deposited from a DMAH precursor over a wide range of thickness. The kinetics were characterized by sheet resistance, RBS and AES measurements. The microstructure evolution was investigated by HRSEM. The nucleation stage was characterized by the formation of discrete Al islands that merged with increasing deposition time. The structure of the nano-grains, as well as the interface of the thick Al film, were studied by HRTEM. This helped to explain the XRD results that on PVD TiN the Al film had a stronger <111> texture than on the other TiN types. The use of light reflectivity as a roughness indicator, showed that the roughness increased with thickness after the merging stage, and some voids were found in the continuous Al films. A change in the deposition hardware of CVD TiN yielded a modified TiN microstructure, which resulted in a CVD Al film with different properties, such as a smoother surface and a lower density of voids.
- N-I.3** 15:00-15:15 STUDY OF Cu CONTAMINATION DURING COPPER INTEGRATION FOR SUB-QUARTER MICRON TECHNOLOGY, **P. Motte**, J. Torres, J. Palleau, F. Tardif, H. Bernard, CEA/LETI, 17 rue des Martyrs, 38054 Grenoble cedex 9, France
Copper contamination in two different dielectric (SiOF and SiO₂) deposited on copper-CVD film was investigated. This study aims to the integration of copper in a dual damascene structure interconnection for sub-quarter micron CMOS technology.
A complete copper contamination profile into the deposited dielectric was measured using SIMS, Total X-ray Reflection Fluorescence (TXRF) and Liquid Phase Decomposition- Atomic Absorption Spectroscopy (LPD-AAS) as complementary characterisation tools.
PECVD process used for both SiOF and SiO₂ imply plasma with fluor. The reactivity of this specie on copper was shown critical for dielectric contamination and copper contact surface. Dependence of dielectric contamination with the deposition process parameters have been investigated. Different cleaning solutions were tested to lower the copper contamination level in the dielectric bulk and at the free surface. In a second step, Cu/SiN/SiO₂ structure characterisation highlighted the thin SiN film barrier performance against copper diffusion in the intermetal dielectric layer.
- N-I.4** 15:15-15:30 THE INTERACTION OF METALS AND BARRIER LAYERS WITH FLUORINATED SILICON OXIDES, **S.E. Kim** and **C. Steinbrüchel**, Department of Materials Science and Engineering and Center for Integrated Electronics and Electronics Manufacturing, Rennselaer Polytechnic Institute, Troy NY 12180, USA
Fluorinated silicon oxide (FSG) films with varying fluorine content were prepared by plasma-enhanced chemical vapor deposition (PECVD) using TEOS, O₂, and either C₂F₆ or NF₃ and characterized with FTIR and nuclear reaction analysis (NRA). Metal films (Al, Cu/1%, Al, Cu) were deposited on the FSG either directly or with a barrier layer (Ta, TaN) between the metal and the FSG. Compositional depth profiles were obtained with XPS and NRA. For Al and Cu/1%Al, diffusion of F atoms through the metal film is rapid at typical annealing temperatures and is noticeable even at room temperature over a period of weeks. At the same time, no specific reaction occurs at the metal-dielectric interface. With Al, the diffused F accumulates on the top surface of the metal film, and no F is present in the bulk of the film. With Cu/1%Al and Cu, no surface enrichment but a larger bulk concentration of F are observed. Neither Ta nor TaN are good barriers against fluorine diffusion. A suitable plasma treatment of the FSG before metal deposition inhibits substantially the diffusion of F into the metal without increasing the dielectric constant of the FSG. Fluorine also diffuses easily through undoped PECVD oxide and thermal oxide.
- N-I.5** 15:30-15:45 OXYGEN LOCALIZATION IN THIN TiN LAYERS OBTAINED BY RAPID THERMAL CVD AT LOW TEMPERATURE, **L. Imhoff**, A. Bouteville, H. de Baynast, J.C. Remy, Laboratoire de Physico-Chimie des Surfaces, ENSAM - CER d'Angers, 2 Bd du Ronceray, BP 3525, 49035 Angers, France
The use of titanium nitride films as diffusion barrier for the IC metallization has been reported by numerous authors. Conventional Physical Vapor Deposition (PVD) methods are going to reach their limits. Chemical Vapor Deposition can be an interesting alternative as long as the deposition temperature is not too high. By Rapid Thermal CVD we obtained thin TiN films on silicon at a deposition temperature as low as 500 °C but chemical analyses reveal oxygen incorporation until 10 %. Such contaminant is well known to play a significant role in the barrier behaviour of TiN layers for the IC metallization.
The aim of this paper is to localize oxygen in the layer : on the surface, at the interlayer TiN/Si, in the grains or at the grain boundaries. For these investigations, scanning electron microscopy (SEM), X-Ray diffraction (XRD) and Auger electron spectroscopy (AES) are carried out.

N-I.6 15:45-16:00

OBSERVATION OF CURRENT POLARITY EFFECT IN STRESSING AS-FORMED SUB-MICRON Al-Si-Cu/TiW/TiSi₂ CONTACTS, Li-Zen Chen, Klaus Y.-J. Hsu, National Tsing Hua Univ., Dept. of Electrical Eng., Hsinchu, Taiwan, ROC

Formation of good silicide contacts becomes more important but difficult as the contact size continues shrinking toward the deep sub-micron regime. At the same time, higher current density which may easily appear in small regions could pose strong impact to the long-term reliability of sub-micron contacts. In this work, high current density stress experiments were conducted on the Al-Si-Cu/TiW/TiSi₂ contacts with the size ranging from 0.5x0.5 μm^2 down to 0.25x0.25 μm^2 . The self-aligned silicide contacts were formed by using collimated sputtering, E-beam lithography, RTA, and RIE techniques. The silicide contacts were sintered at 400°C for 30 minutes. Cross-bridge Kelvin resistor structure was formed for electrical stressing and contact resistance measurement. One-way and two-way stressings were performed at high current density ($\sim 10^7$ A/cm²) and the contact resistance was measured periodically at low current density during the stress to monitor the evolution. It was found that the initial resistance of as-formed contacts was higher than expected. This is probably due to the difficulty of forming good interfaces by sputtering and that the sintering temperature may be not high enough to smear out the imperfection. The stressing was found to anneal the contacts. With electrons flowing from metal layer into the contact window (normal current), the contact resistance was reduced more efficiently than with reverse current of the same density. Stressed first by reverse current then by normal current, the resistance showed a two-step reduction with a significant transition at the switch of current polarity. For prolonged stressing, the contacts were degraded and the reverse current induced more severe damage (even open-circuit in some cases.) These observations indicate strong electromigration effect at the small contacts.

N-I.7 16:00-16:15

COBALT SILICIDE THERMAL STABILITY: FROM BLANKET THIN FILM TO SUBMICROMETER LINES, A. Alberti, M.G. Grimaldi, E. Rimini, Physics Department, Catania University, Italy, F. La Via, CNR-IMETEM, Catania, Italy, S. Ravasi, ST Microelectronics, Catania, Italy

The submicrometer lines and the blanket thermal stability of 100 nm cobalt disilicide reacted on pre-amorphized Chemical Vapour Deposited silicon 5 inches wafer has been studied. The high temperature RTP windows chosen lies between 850°C and 1100°C. The annealing effect on the silicide linewidth and on the grain size distribution was studied through TEM plan-view, while the surface lines roughness was measured with a Atomic Force Microscope (AFM). Bridge resistors down to 0.15 μm has been used to measure the stripes resistance and a strong correlation between lines resistance and morphology change during the high temperature annealing (RTA) has been found. A linear increase of the resistance versus annealing time was observed at any temperature in both blanket and patterned silicide. An activation energy equal to ~ 4 eV for both degradation process has been obtained. Nevertheless, the resistance increase is faster in patterned than in blanket silicide films. In blanket film the degradation process is described in terms of uniform agglomeration through the silicide thickness: the increase of sheet resistance can be modelled taking into account the thickness dependence of the resistivity for thin films. In patterned film, instead, the degradation is a no uniform process because of the lateral confinement: the increase of the lines resistance is essentially a geometric effect.

Wednesday, June 17, 1998

Mercredi 17 juin 1998

Afternoon

Après-midi

SESSION II - Metallizations, Part 2

- N-II.1** 14:00-14:30 - Invited - SUBMICRON Cu-METALLIZATIONS, **J. Torres**, GRESSI, CENT/CEA, Grenoble, France
- N-II.2** 14:30-14:45 AN INVESTIGATION INTO THE PERFORMANCE OF DIFFUSION BARRIER MATERIALS AGAINST COPPER DIFFUSION USING METAL-OXIDE-SEMICONDUCTOR (MOS) CAPACITOR STRUCTURES, **V.S.C. Len**, N. McCusker, D.W. McNeill, B.M. Armstrong and H.S. Gamble, Dept. of Electrical Engineering, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland
Copper-based interconnects are expected to be in widespread use for ULSI fabrication after the year 2000 due to copper's low resistivity and high electromigration resistance. It has been widely reported that copper diffuses quickly through dielectric layers and silicon at elevated temperatures and deteriorates the performance of the underlying devices. Thus to prevent Cu diffusion, a diffusion barrier is necessary. Cu / SiO₂ / Si capacitors were fabricated, with and without barrier layers between the copper and the oxide. The dielectric properties of the 100nm thick thermal SiO₂ were monitored for a range of high temperature stress conditions. Capacitance-Voltage and current-voltage techniques were used to characterise the electrical properties of the dielectric film. Control capacitors without barrier layers exhibited dielectric degradation after a 60 s 400°C rapid thermal anneal. This effect is aggravated by an increase in annealing temperature resulting in a 3.4V flat-band shift following a 700°C 60 s anneal. Diffusion borders of Ti, W, Ta and their nitrides were assessed in terms of diffusion barrier efficiency and thermal stability. Results obtained will be at the conference.
- N-II.3** 14:45-15:00 SILICIDE REACTION OF Co WITH Si_{0.999}C_{0.001}, **S. Teichert**, M. Falke, H. Giesler, G. Beddies and H.-J. Hinneberg, Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany, G. Lippert, J. Griesche and H.-J. Osten, Institute of Semiconductor Physics Frankfurt/Oder, Walter-Korsing-Strasse 2, 15230 Frankfurt, Germany
The disilicide of Co is a promising metallic material for the submicron technology. The advantage of this material is the low specific resistivity as well as the low preparation temperature. A further downscaling in the Si technology requires in addition to lower process temperatures effective measures to avoid changes of the doping profiles. One method for trapping doping profiles is the use of a small amount of carbon in the Si-wafer. In this work we compare the reaction of a thin Co film with Si_{0.999}C_{0.001}(001) and Si(001). The Si_{0.999}C_{0.001}(001) was prepared by a MBE method under UHV conditions. The Co films were deposited by e-beam evaporation in a second UHV equipment. The reaction of the Co films with the substrate was performed by isochronal rapid thermal annealing at different temperatures. The samples were analysed by RBS and measurements of the electrical resistivity at room temperature in dependence on the applied annealing temperature. For Si_{0.999}C_{0.001}(001) an increase of the temperature of the disilicide formation compared with Si(001) has been found. Differences of the resulting CoSi₂ prepared under identical annealing conditions have been investigated in more detail by the use of TEM and temperature dependent measurements of the electrical resistivity.
- N-II.4** 15:00-15:15 CHARACTERISTICS OF SPUTTER-DEPOSITED TiN, ZrB₂, AND W₂B DIFFUSION BARRIERS FOR ADVANCED METALLIZATIONS TO GaAs, **M. Guzewicz**, A. Piotrowska, E. Kaminska, K. Golaszewska, Institute of Electron Technology, Al.Lotnikow 46, 02668 Warsaw, Poland, A. Turos, Institute for Nuclear Studies, Warsaw, Poland
As the critical dimensions for III-V semiconductor devices shrink, new metallization technologies are required. One of the solution to this problem is that in which a barrier material is interposed between the contact metallization and the metal overlayer. In this work resistivity, stress, and barrier properties of TiN, ZrB₂, and W₂B thin films have been investigated, with the aim of improving the reliability of gold-based metallization to GaAs. TiN films were prepared by reactive r.f. bias magnetron sputtering from a Ti target; ZrB₂, and W₂B - from composite ones. Sheet resistance was measured using four-point probe system. The Tencor FLX-2320 system was used for thin film stress measurements. Barrier properties were determined by RBS. The effect of the process parameters on the properties of barrier films will be discussed and the combination of variables which lead to optimum barrier properties will be indicated.
- N-II.5** 15:15-15:30 TEM STUDIES OF THE MICROSTRUCTURE EVOLUTION IN PLASMA TREATED CVD TiN THIN FILMS USED AS DIFFUSION BARRIERS, **S. Ikeda***, N. Bourhila, B. Chenevier, R. Madar, Laboratoire des Matériaux et Génie Physique, URA CNRS 5628, ENSPG, BP46, 38402 Saint-Martin d'Hères, France and J. Palleau, J. Torres, GRESSI CNET/FT, Chemin du Vieux Chêne, BP 98, Meylan, France *also: National Research Institute for Metals, Sengen, Tsukuba, Ibaraki 305 Japan
A series of TiN films used as diffusion barrier in the semiconductor industry have been prepared by Chemical Vapor Deposition (CVD). They have been synthesized by alternating growth and ion-plasma application. Transmission Electron Microscopy (TEM) observations of the films indicate a 100 film texture if the plasma power is low and its duration is short. If plasma parameters are increased, the texture turns to 110. Films obtained without plasma treatment are made of randomly oriented nanocrystallites. The texture evolution and its influence on the barrier properties have been investigated. It could be explained in terms of nucleation processes controlled by surface energy for low plasma parameter values and by a plasma effect for higher parameters.

SYMPOSIUM N

N-II.6 15:30-15:45

INVESTIGATION OF IMP Ta/TaN AS DIFFUSION BARRIER LAYER BETWEEN COPPER AND SILICON DIOXIDE, G. Chuang, K.M. Yin, F.R. Chen, L. Chang, J.J. Kai, Department of Engineering and System science, National Tsing-Hua University, Taiwan, R.O.C. and H. Zhang, B. Chin, F.S. Chen, Metal Deposition Group, Applied Materials, Santa Clara, USA

Copper has the characteristic of lower bulk electrical resistivity and better resistance to electromigration than aluminum in ULSI. However, choosing a proper material as diffusion barrier layer between copper and most contact materials is not easy for its high mobility in metals and semiconductors. In this work, ionized metalization process (IMP) Ta/TaN thin film (10~35nm of thickness) is selected as diffusion barrier layer between Cu and SiO₂. This work utilized the specimens with and without trenches. The specimens with trenches were under thermal failure test; the others were under bias temperature stress (BTS) test. After the failure test, by nano-beam X-ray energy dispersive spectrometer (XEDS), Field Emission Gun TEM, and energy-filter, analysis for both specimens showed silicon has diffused into Ta/TaN layer. In specimens with trenches, Ta/TaN film is found to contact directly with silicon substrate for diffusion of silicon and oxygen in SiO₂ into Ta/TaN layer. Reacted interlayers have also been observed between Cu and Ta/TaN thin film for both specimens. We believe the thin film could be a compound formed by copper, tantalum, and silicon. The detail analysis of the interfacial reaction of the Cu metal with the Ta/TaN barrier layer will be presented in the conference.

N-II.7 15:45-16:00

TEXTURING, SURFACE ENERGETICS AND MORPHOLOGY IN THE C49-C54 TRANSFORMATION OF TiSi₂, L. Miglio, M. Iannuzzi, M.G. Grimaldi*, F. La Via, F. Marabelli***, S. Bocelli****, S. Santucci*****, A.R. Phani*****, Istituto Nazionale di Fisica della Materia, Unità di Milano, *Catania, **Pavia, ***L'Aquila, ****IMETEM-CNR di Catania, Italy**

One open question in the phase transformation of TiSi₂ from high resistance (C49) to low resistance (C54) structure is the texturing of the parent and target phases, depending on the substrate conditions (crystalline Si(001) or polysilicon) and the dimensionality (blanket film or narrow lines). This issue is important in predicting the quality of interconnections and in explaining the microstructural evolution in the surface roughness during the transformation. We analyzed by XRD technique the texturing of our samples, as grown by solid state reaction after UHV deposition of a thin Ti film (17 nm). We compared the results to the estimation of the surface energies by tight binding molecular dynamics for the most interesting orientations (131), (311), (040). The evolution in surface roughness has been analyzed by AFM statistics and light diffusion measurements. We propose a model which could explain the evolution in surface roughness on the basis of columnar grain growth and preferential grain orientations. It turns out that the samples grown on Si (001) do behave rather differently with respect to the polysilicon ones.

N-II.8 16:00-16:15

ELECTROMIGRATION IN COPPER INTERCONNECTS, N. McCusker, V.S.C. Len, D.W. McNeill, B.M. Armstrong and H.S. Gamble, Dept. of Electrical Engineering, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland

Copper is expected to come into widespread use during the next few years, in submicron metallisation structures due to its improved conductivity and reliability over Aluminium alloys. The incorporation of copper into logic devices has been cautious due to its potential diffusion and adhesion problems. A suitable adhesion/diffusion barrier layer must be incorporated to encapsulate the copper. In this study, RF magnetron sputtered ($\rho = 1.9 \mu\Omega\text{cm}$) has been deposited on possible barrier layers of Ti, W, Ta and nitrides. AFM analysis has been used to show how the barrier layers influenced the growth of the copper layers. The dependence of grain size and uniformity on the sputtering parameters was studied. The subsequent effect on electromigration reliability was also assessed. Mean-time-to-failure (MTF) tests were carried out on multi-line structures in an inert gas ambient. These have shown the superiority of copper over aluminium and the beneficial effects of passivation and post deposition annealing. AFM studies have been used in an attempt to understand the different voiding processes apparent in copper and aluminium.

Thursday, June 18, 1998

Jeudi 18 juin 1998

Morning

Matin

SESSION III - Lithography

- N-III.1** 10:30-10:45 **SPUTTERED TUNGSTEN FILMS ON POLYIMIDE, AN APPLICATION FOR X-RAY MASKS**, J. Ligot, S. Benayoun, J.J. Hantzpergue, J.C. Remy, Laboratoire de Physico-Chimie des Surfaces ENSAM-CER d'Angers, 2 Bd du Ronceray, BP 3525, 49035 Angers, France
Among processes of lithography for submicron technologies, x-ray lithography shows the great advantage of high resolution. In the fabrication of x-ray masks, tungsten (W) is one of the alternate absorber materials that can be used instead of gold, but it requires to obtain a low stress film with high density. Tungsten films were deposited on Kapton and Upilex polyimides using a triode discharge system. The dependence of thin W films properties on the working argon pressure is reported. X-ray diffraction, AFM and radius curvature measurements were used to characterize the coatings in terms of microstructure and mechanical properties. Residual stress and density were found to be significantly dependent on the argon pressure. Microstructural analysis indicated that with increasing thickness, the grain size increased and the proportion of metastable phase, β -W which changes its stress under high-temperature annealing, could vary in a wide range. The adhesion of W to polyimide assessed with scratch testing technique seemed very acceptable.
- N-III.2** 10:45-11:00 **POLYMER ISSUES IN NANOIMPRINTING TECHNIQUE**, F. Gottschalch, Th. Hoffmann, C.M. Sotomayor Torres, Institute of Materials Science, Department of Electrical Engineering; H. Schulz, H.-Ch. Scheer, Micropatterning in Electrical Engineering, Department of Electrical Engineering, University of Wuppertal, Fuhlrottstr. 10, 42097 Wuppertal, Germany
Fabrication of nm-scaled devices will require reliable large patterning techniques, Optical lithography is expected to be limited to 150 nm pattern size. Techniques like X-ray and ion beam lithography are rather expensive and electron beam lithography despite its application in production suffers from its low throughput. In the last years novel approaches based on imprint technologies have been proposed. In one of these techniques a polymer thin film is patterned by imprinting with rigid stamp above the glass transition temperature T_g of the polymer (nanoimprinting). One of the mayor problems to address is sticking between the polymer and the stamp. Nevertheless, imprints down to 100 nm size were performed successfully using a thermoplastic spin coated on a silicon wafer. The results demonstrate the potential of the technique. Recent results with respect to polymer type, stamp material, temperature range, pattern size and profile, and the imprint time will be reported. The problems and possibilities to overcome them will be discussed.
- N-III.3** 11:00-11:15 **NANOMETER SCALE LITHOGRAPHY ON SILICON, TITANIUM AND PMMA RESIST USING SCANNING PROBE MICROSCOPY**, E. Dubois, J.-L. Bubbendorff, IEMN/ISEN, UMRS CNRS 9929, 59652 Villeneuve d'Ascq, France
STM and AFM nanolithography techniques based on local oxidation of silicon/titanium and electron beam exposure of PMMA are described. It is shown that 10 nm resolution can routinely be achieved using tapping-mode AFM-based anodisation of silicon and titanium operated in air. The thickness and width of oxide stripes are studied as a function of the applied probe-sample voltage, the speed of the probe and the setpoint (current, applied force and vibration amplitude) for STM, AFM contact and tapping, respectively. Exposure of PMMA resist (950K,3%) is also demonstrated using contact-mode AFM to control the tip/surface interaction through a constant force and field emission of electrons to expose the resist. The exposure dose is controlled by constant current injection. The sensitivity of the lithography resolution with the electron dose, beam current and tip speed is discussed. The use of low-energy electrons (10-100 eV) eliminates proximity effects.
- N-III.4** 11:15-11:30 **DEEP SUBMICROMETER PATTERNING OF EPITAXIAL CoSi_2/Si (100) BY LOCAL OXIDATION**, Q.T.Zhao, M. Dolle, L. Kappius, St.Mesters and S.Mantl, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, 52425 Jülich, Germany
The deep submicrometer patterning of the crystalline CoSi_2 layers on Si(100) by local oxidation was studied in this paper. Epitaxial CoSi_2 layers with thicknesses around 20nm were grown on Si(100) by molecular beam allotaxy. Oxide and nitride layers were deposited on the surface of the silicide and subsequently patterned along the $\langle 110 \rangle$ direction by optical lithography and dry etching. Thermal oxidation was then performed at a temperature of 950°C in dry O_2 ambient using the rapid thermal processing system. During oxidation SiO_2 forms on the unprotected regions of the CoSi_2 layer. The silicide in this region is pushed into the substrate. Near the edges of the nitride mask the silicide layer thins and finally separates from the protected part. Using this patterning method gaps with a width of less than 100nm between the two silicide layers could be obtained. It was shown that the separation gap is not only dependent on the oxidation parameters, but also on the thickness and the width of the nitride mask due to the possible stress effects. Possible application of this technique is also discussed.

SYMPOSIUM N

N-III.5 11:30-11:45

HOLOLITHOGRAPHY : HOLOGRAPHY OF PARTICLE BEAMS : PRINCIPLES, POSSIBILITIES AND PRESENT REALISATIONS, M. Grossmann, S. Guedda, Université L. Pasteur, 67000 Strasbourg, France and H. Fujita, Chuo-Gakuin University, Abiko City 270-1163, Japan

Coherent particle beams give the possibility of recording informations by interferences.

Historically, Gabor was brought to holography by problems of aberrations of electron beams in electron microscopy. But the de Broglie wavelengths of usually available particles (electron neutrons, ions or atoms) are extremely small, in the ranges of x or gamma-rays. So holography cannot cross such a big wavelength gap and the ensuing problems (materials with sufficient resolution for recording and development, aberrations at restitution etc ...). Charged particles have also an inconvenient property of repulsing each other. Which does not make it easy to use them to create a parallel beam ... Recently Laser and atom physicist have started creating beams of neutral atoms which have wavelength in a (not too in-) convenient range.

Interferences have been recorded and diffraction reconstruction has been obtained. The way is now open for developments. To this end we need improvement of facilities. We discuss the obtained results, the improvements needed in the experimental set-up and the exciting possibilities : recording objects (and not light) and reconstructing object (and not images). By analogy with presently well developed technology of stereolithography we propose to call this new technology : Hololithography.

11:45-14:00

LUNCH

Thursday, June 18, 1998

Jeudi 18 Juin 1998

Afternoon

Après-midi

SESSION IV - Poster Session

14:00-16:00

See programme of this poster session p. N-10 to N-13.

Friday, June 19, 1998
Vendredi 19 Juin 1998

Matin
Morning

SESSION V - Nanomaterials

- N-V.1** 9:15 :9:45 - Invited - POROUS SILICON NANOSTRUCTURES, **V.P. Parkhutik**, Dpto. De Termodinamica Aplicada, Universidad Politecnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain
- N-V.2** 9:45-10:00 THE SMTAGB (SYMMETRIC-MEDIUM-TILT-ANGLE-GRAIN-BOUNDARY) AS A NANOMETRIC SUPERSTRUCTURE, **H.F. Mataré**, Internat. Solid State Electronics Consultants, Malibu, CA 90265, USA
After definition of the crystallographic parameters of the SMTAGB, the particular mechanical and electronic features will be discussed, with emphasis on the longitudinal, degenerate conductivity and the vertical barrier layer. The dense packing due to overlap of dilatational and compressional zones, causes clean growth, without a second phase and with high energy which gives these structures valuable properties. The high density of dangling bonds with a resultant electron plasma, can be treated as a system of coupled quantum wires. The use in HT (high temp.) superconductors (I_c -enhancement) and in Josephson junctions for SQUIDS as well as the new electrooptic and transistor applications will be described.- The description in terms of Wannier-Stark ladders is related to the outstanding optoelectronic features. Recent measurements of IR-absorption shifts and low temperature photoconductivity are discussed.
- N-V.3** 10:00-10:15 TWO DIMENSIONAL NANOWIRE FORMATION ON Si SUBSTRATE USING SELF-ORGANIZED NANOHOLES OF ANODICALLY OXIDIZED ALUMINUM, **S. Shingubara**, O. Okino, H. Sakaue, and T. Takahagi, Hiroshima University, Dept. of Electrical Engineering, Kagamiyama 1-4-1, Higashi- Hiroshima 739-8527, Japan
Materials processing using self-organization phenomena is promising to fabricate large area array of nanometer structures, since there is a fundamental difficulty in throughput by conventional lithographic techniques. Anodic oxidation of aluminum (Al) is one of the typical self-organization which can produce two dimensional triangle lattice of nanometer structures [1,2]. The present work is the first report of nanowire array which is directly grown on Si substrate by the usage of Al anodic oxidation.
In order to fabricate nanowire array on Si, at first a very thin (10 nm) SiO_2 was formed on Si surface, and Pure Al film was sputtered on SiO_2 . Then two step anodization [1] was carried out for the Al film at 40 V and 25 nm diameter nanohole array of 150 nm depth were formed. Cu nanowires were successfully deposited in these nanoholes uniformly by electroless deposition, and finally Cu wire array of 40 nm diameter were grown on Si substrate. The reason why Cu wire diameter was slightly larger than hole diameter was that aluminum oxide was dissociated by Cu electroless solution. Further investigation to deposit metal wires in nano holes by electroplating after removal of SiO_2 film by anisotropic dry etching is in progress.
[1] H. Masuda, and K. Fukuda, Science vol.268 (1995) 1466.
[2] S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, and T. Takahagi.
- N-V.4** 10:15-10:30 COULOMB BLOCKADE: POISSON VERSUS PAULI IN A SILICON QUANTUM BOX, **L. Palun**, LETI, CEA, 17 Rue des Martyrs, 38054 Grenoble Cedex 9, G. Lamouche and G. Fishman, Laboratoire de Spectrométrie Physique - UMR C5588, Université Joseph Fourier - Grenoble 1 - CNRS, BP 87, 38402 Saint-Martin d'Hères Cedex, France
Devices using Coulomb blockade effect, such as metallic single electron transistors, are well-known. The devices must both have MOSFET compatibility and be room temperature operating for microelectronics, i.e. in silicon devices. Therefore Coulomb energy $e^2/2C$ must be five-to-ten times larger than room temperature energy kT to be effective. This implies quantum dots, namely nanometer dots. A few nanometer silicon dot exhibits Coulomb blockade effect and also the quantization of energy levels. Thus this last effect must properly be taken into account.
Here we present a simple model which combines i) an effective-mass description for the particles, ii) a square potential for the silicon dot, and iii) a Poisson (Hartree) approach for the electrostatic potential. In other words the energy quantization is calculated via a Poisson-Schrödinger equation. This allows us to describe the additional energy due to level quantization. We are then able to discuss the relation with the orthodox theory (Likharev) describing Coulomb blockade. Our simple model is then compared with a more sophisticated one including the Pauli principle. Finally we show that the simple model can be easily included in microelectronic simulators and therefore can be very effective to predict new properties of future quantum devices.
- 10:30-11:00 **BREAK**
- N-V.5** 11:00-11:15 SPECTRAL CHARACTERIZATION OF POROUS SILICON BASED PHOTO-DIODES, **R.J. Martin-Palma**, R. Guerrero-Lemus, J.D. Moreno and J.M. Martinez-Duart, Departamento de Fisica Aplicada, C-12, Universidad Autonoma de Madrid, 28049 Cantoblanco, Madrid, Spain
Porous silicon (PS) based Schottky structures were formed by depositing gold (Au) contacts onto the PS surface. PS was formed from p-silicon substrates under different formation parameters (current density, time of anodization, illumination, etc.), so PS layers with different porosities and thicknesses were obtained. The photoelectronic properties of the PS-based diodes are reported in this work. It was determined the responsivity and the quantum efficiency of these structures in the 200-2500 nm wavelength range, finding a significant response in the visible and near infrared parts of the spectrum. It has been observed a different behaviour of those diodes depending on the porosity and thickness of the PS layer. It has also been studied the spectral response from different diodes in which the PS surface has been modified by applying different post-formation chemical treatments and from diodes in which semitransparent conducting films (metals and semiconductors) have been deposited onto the PS layer, obtaining a significant improvement in the photoelectronic properties.

SYMPOSIUM N

N-V.6 11:15-11:30

THE FORMATION OF NARROW NANOCLUSTER BANDS IN Ge-IMPLANTED SiO_2 -LAYERS, J. von Borany, K.-H. Heinig, A. Markwitz, and B. Schmidt, Institut für Ionenstrahl-Physik und Materialforschung, Forschungszentrum Rossendorf, PO Box 51 01 19, 01314 Dresden, Germany

The concept of nonvolatile memories based on semiconductor nanoclusters within the gate oxide of a memory cell requires equal-sized nanoclusters very close to the Si/SiO₂ interface. Then, the charge exchange between the substrate and the cluster will occur via direct tunneling.

This contribution describes the formation of narrow bands of crystalline nanoclusters by using implantation of $10^{16}\dots 10^{17} \text{ Ge}^+/\text{cm}^2$ into 100 nm thermally grown SiO₂-layers and subsequent annealing (500-1100°C, N₂). The Ge depth profile, the spatial distribution of the nanoclusters and the cluster size have been found to depend strongly on the implantation and annealing conditions which have been investigated in detail by RBS, STEM-EDX and cross-sectional TEM, respectively. Although the implanted Ge depth profile is distributed over almost the whole SiO₂ layer, a very narrow band (typical width 5 nm) of Ge nanoclusters very close but well-separated to the Si/SiO₂-interface is formed by self-organization under specified annealing conditions. Possible mechanisms for this self-organization process will be discussed including nucleation phenomena, Ostwald ripening and defect-stimulated interface processes. Simple MOS-structures were prepared and the effect of charge storage inside the clusters has been derived from CV-characteristics.

N-V.7 11:30-11:45

INFLUENCE OF POST-ETCHING TREATMENTS IN THE PHOTOLUMINESCENCE OF POROUS SILICON, R. Guerrero-Lemus, J.D. Moreno, F.J. Martin-Palma and J.M. Martinez-Duart, Dpto de Fisica Aplicada, Univ. Autonoma de Madrid, 28049 Madrid, Spain

This work is focused to the study of the stabilization of the photoluminescent properties of porous silicon (PS). For this purpose, as-formed PS samples were subjected to different post-etch treatments. Photoluminescent excitation spectra were used to obtain the indirect band gaps, yielding practically the same values for PS films having undergone different surface annealing and post-etch treatments. In addition, the excitation spectra show a blueshift with aging for the different samples, which has been related to the initial amount of oxygen present in the porous surface as detected by XPS and FTIR. The variation of the intensity of the excitation spectra with aging has also been studied and can be associated to carbon contamination. The emission spectra of the different samples have been also studied. The results are interpreted in terms of quantum size effects in PS and the influence of the surface composition.

N-V.8 11:45-12:00

SYNTHESIS OF CdS NANOPARTICLES IN MOR TYPE ZEOLITES, H. Villavicencio Garcia*, M. Hernandez Velez*, O. Sanchez Garrido**, J.M. Martinez Duart*** and J. Jimenez Lopez****, *Grupo de Zeolitas y Propiedades Dielectricas en Solidos, L.S.P. " E.J. Varona ", C. Libertad, Marianoa, C. de la Habana, Cuba ; **Instituto de Ciencia de Materials, CSIC, Madrid, Spain, ***Dpto de Fisica Aplicada, Universidad Autonoma de Madrid, Spain, ****Dpto de Fisica de la Material Condensada, Universidad de Valladolid, Spain

Hydrothermal synthesis and characterization of CdS particles into zeolite cavities is reported in this work. We have obtained both a synthetic MOR type zeolite as a matrix (host) and the CdS particles via hydrothermal synthesis. As-synthesized zeolites samples were doped with CdS at different interchange ratios. The resulting materials were characterized by X-ray diffraction, Raman spectroscopy, optical absorption in the visible range, X-ray fluorescence analysis and N₂ physical adsorption. The results allow us to confirm the amorphization of the starting zeolitic structures and the presence of semiconducting inclusions in their pores and cavities. The size of the CdS semiconducting crystallites is quite large, their distribution range from 20 to 60 nanometers. The optical features of the samples showed some quantum confinement effects, like the variation of the band gap from 3.6 to 2.59eV, depending on the CdS nanoparticles size.

12:00

LUNCH

END OF SYMPOSIUM N

SYMPOSIUM N
SYMPOSIUM N
POSTER SESSION

Thursday June 18, 1998
Jeudi 18 juin 1998

Afternoon
Après-midi

SESSION IV - Poster Session
14:00-16:00

- N-IV/P1** THERMAL CONDUCTIVITY OF THE NANOMATERIALS, J. Marciak-Kozłowska, Institute of Electron Technology, Al. Lotników 32/46, 02-668 Warsaw, Poland
For nanomaterials the quantum heat transport equation was formulated in paper [1]:
$$\tau \delta^2 T / \delta t^2 + \delta T / \delta t = h m V^2 T (1)$$
where T is the temperature, τ - relaxation time and h/m denotes the quantum heat diffusion coefficient. In this paper will be shown that the thermal conductivity k for nanomaterials do not depends on the temperature T and equals:
$$k = h \rho c / m \quad (2)$$
where ρ is the density and c denotes the specific heat. Recent measurements of the nanostructures GaAs/AlAs show very weak dependence of k on temperature [2].
[1] J. Marciak-Kozłowska et al., Found. Phys. Lett. 9 (1996) 235
[2] W.S. Capinski, H.J. Maris, Physica B219/220 (1996) 699
- N-IV/P2** HYDROGEN REDISTRIBUTION AND DEGRADATION OF THIN SILICON DIOXIDE AND SILICON NITRIDE FILMS DURING ELECTRON INJECTION AND THERMAL TREATMENT IN HIGH FIELDS, G.V. Gadiyak, Institute of Computational Technologies, Russian Academy of Sciences, Siberian Division, Prospekt Lavrentjeva 6, 630090 Novosibirsk, Russia
A macroscopic transport models for i) the hydrogen redistribution in a silicon dioxide and silicon nitride, ii) electron-hole transport and accumulation of charge in these films during electrical stress thermal treatment are proposed in this paper. The set of equations for the first model consists of two diffusion equations for the "free" atomic and molecular hydrogen, diffusion equation for atomic nitrogen and rate equations for the bound hydrogen and nitrogen and dangling bonds (hydrogen trap). The second model considers the kinetics of charge accumulation on the existing and new trapping centers created during electrical stress or thermal treatment using rate equations for electrons and holes and the Poisson equation. The fitting parameters of the model have been found. The results have been compared to experimental data.
- N-IV/P3** FOCUSED ION BEAM STRUCTURING OF Si AND Si/CoSi₂-HETEROSTRUCTURES USING ADSORBED HYDROGEN AS A RESIST, H. Fuhrmann, M. Döbeli, R. Mühle, Paul-Scherrer-Institut, c/o IPP, ETH-Hönggerberg, 8093 Zürich, Switzerland
We have used adsorbed H at the passivated surface of Si(100) as a resist layer for focused ion beam irradiation. The H-layer was locally removed by the irradiation with 15keV Ga⁺ ions. Subsequent exposure of the samples to air resulted in the formation of a natural oxide where the H had been removed. This natural oxide was used as a mask in an KOH etch, yielding Si bars with widths down to 100 nm. We compared the critical irradiation doses for this process with the critical dose for samples which had not been H-passivated prior to irradiation and found that the depassivation process has a critical dose of $3 \cdot 10^{13} \text{ cm}^{-2}$. This is almost two orders of magnitude lower than the critical dose for the known etch stop caused by high Ga concentrations in silicon, for which critical implantation doses of $1 \cdot 10^{15} \text{ cm}^{-2}$ have been measured.
We then applied the depassivation process to an MBE-grown (4 nm Si / 4 nm CoSi₂ / Si(100)) heterostructure. In this case, the 4 nm Si layer on top was removed outside of the irradiated regions by the KOH etch. In a second etch process, the CoSi₂ layer was removed by HF. CoSi₂ lines as narrow as 160nm were produced. The height profiles were checked by AFM measurements after both etches, confirming the model of depassivation.
Further experiments deal with the critical doses for depassivation using Si⁺ ions instead of Ga⁺ ions.
- N-IV/P4** KINETICS OF ULTRATHIN SiO₂ FILMS GROWTH IN OXYGEN, A.A. Evthukh, V.G. Litovchenko, A.Yu. Kizijak, Yu.M. Pedchenko, Institute of Semiconductor Physics, 45 Prospekt Nauki, Kiev 252650, Ukraine
The Si-SiO₂ systems with ultrathin SiO₂ currently are important for submicron electron devices. The kinetics of thermal oxidation in temperature range 700-850°C have been investigated. In this study the silicon wafers (100) and (111) orientation, n- and p- type with doping level $1 \times 10^{15} \text{ cm}^{-3}$ and $3.5 \times 10^{14} \text{ cm}^{-3}$ respectively were used. The thickness range with $d < 20 \text{ nm}$ ("anomalous oxidation region") have been studied in detail. In investigated oxidation conditions and thickness range the three region of oxide growth can be seen. First one is fast initial oxidation that occurs while loading of the wafers in the furnace. Second region is growth till (5.0-7.0) nm and third one is growth after (5.0-7.0) nm. In each region the growth kinetics can be described by equation $x = s + at^b$ with own s , a , b coefficients. For all experimental curves the features in kinetic growth are observed in thickness range (5.0-7.0) nm. This feature is more clearly observed in case of least rate growth.
The feature in thickness range of (5.0-7.0) nm is connected with structural rearrangement of SiO₂. Such transformation is a result of viscous flow of SiO₂ matter caused by mechanical stress in Si-SiO₂ system due to discrepancy of molecular volumes of silicon and silicon dioxide.
- N-IV/P5** PROCESSING AND CHARACTERISATION OF SOL-GEL DEPOSITED Ta₂O₅ AND TiO₂-Ta₂O₅ DIELECTRIC THIN FILMS, A. Cappellani Siemens AG, ZT ME 1, Corporate Technology, Otto-Hahn-Ring 6, 81730 Munich, Germany; J.L. Keddie, N.P. Barradas and S. Jackson, University of Surrey, Guildford, GU2 5XH Surrey, UK
High-dielectric thin films of Ti doped Ta₂O₅ were deposited on n+ type silicon substrate using the spin-on sol-gel process. Following deposition, films were processed at temperatures between 600 and 900°C using rapid thermal annealing in N₂O.
Spectroscopic Ellipsometry (SE) and Rutherford Backscattering Spectrometry (RBS) were used to determine the thickness and the composition of the thin films and of the interfacial reaction layers. Metal-Insulator-Semiconductor capacitor structures were fabricated and Impedance-Frequency measurements were carried out to measure the dielectric constant of the deposited films.
Results from both RBS and SE showed that an SiO₂ layer is formed at the Ta₂O₅/Si interface during processing, while the titanium doping inhibits the kinetics of its formation. We found that the dielectric constant of the highly Ti-doped Ta₂O₅ film was 78% greater than that of Ta₂O₅ sol-gel film processed under similar conditions.

- N-IV/P6** THE INFLUENCE OF ARC PLASMA JET TREATMENT ON CHARGE STATE OF MOS STRUCTURE, V.V. Andreyev Bauman Moscow State Technical University, Kaluga Branch. 4, Bazhenov St., Kaluga, 248600, Russia; J.O. Lichmanov RIC "Lepton" Moscow, 103489, post box 19, Russia; V.M. Maslovsky, Zelenograd Research Physical Problems Institute. Moscow, 103460, Russia; G.Ya. Pavlov, Scientific industrial Concern "Scientific Center", Moscow, 103460, Russia

The charge state changes of Si-SiO₂-Si* (poly-silicon) structures due to electric arc plasma jet treatment (APJT) have been investigated. The test MOS-structures (Si O₂ thickness was 90 nm) manufactured on phosphorus-doped n-type wafers. The Ar-air plasma flow was formed by multiple jet electric arc generator at atmospheric pressure [1].

After APJT the shift of capacitance - voltage (C-V) characteristics was correspond to the formation of positive charge in Si O₂. The total negative charge in Si O₂ have been registered by the shift of the current-voltage (I-V) characteristics along the voltage axis (ΔV_1) during the high-field tunnel electron injection from silicon when the direct current amplitude was increased. But after the end of current pulse this negative charge was diminished to zero during some seconds. This APJT effect of ΔV_1 increase during injection was decreased in half in 3 months.

[1]. V.M. Maslovsky, G.Ya. Pavlov. MRS Symp. Proc. 391, 139 (1995)

- N-IV/P7** MOLECULAR DYNAMICS SIMULATION OF VOID IN AN ALUMINIUM INTERCONNECTION CONTAINS TRIPLE POINTS GRAIN BOUNDARIES, S. Abdeslam and S. Shingubara, Plasma Electronics Laboratory, Department of Electrical Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi Hiroshima, 739, Japan

Void movement due to electromigration under high stress current density in an aluminium line contains triple point grain boundary will be investigated using molecular dynamics simulations. The empirical Morse potential and the ballistic model for an electron wind force have been employed [1].

At first, we consider two triple points grain boundary structures. We assume [111] twin boundary and [001] twin boundary. There are periodic boundaries at x and z directions and fixed boundary at y direction. There is mirror symmetrical arrangement in y direction. Before we will have investigate the stability of void under an uniform strain and its behavior in the presence of high current density we must resolve the questions of boundary conditions and the stability of the structure of triple points after many thousand time steps run.

[1]: Shoso Shingubara, Isao Utsunomiya, Takayuki Takahagi. Applied Surface Science 91 (1995) 220 - 226

- N-IV/P8** INVESTIGATION OF PROPERTIES OF POROUS SILICON EMBEDDED WITH ZnSe and CdSe, A.I. Belogorokhov, Institute of Rare Metals, Leninsky prosp., 156-517, Moscow 117571, Russia, L.I. Belogorokhova, Moscow State University, Physics Department, S. Gavrilo, Institute of Materials for Electronics, Russia

The formation of the ohmic contacts to a porous medium such as porous silicon (PS) is, still a challenging problem. There is experimental evidence that this problem can be solved by embedding the PS with II-VI semiconductor. Here we investigate photoluminescence (PL), cathodoluminescence, FTIR and Raman spectra of these new porous materials.

Despite extensive efforts, the nature of the visible PL from PS, whether due to the spatial and quantum confinement in the Si crystallites, to surface states, or to various Si compounds, is still intensely debated. In this work, an attempt is made to reveal the relationship between the PS microstructure, PL and FTIR properties and the surface chemical composition, especially the changes in hydrogen and oxygen termination of pores. We compare the PL, Raman and FTIR spectra of the pure PS area of samples with those obtained from the embedded areas on the same wafer. The results are consistent with the stabilisation of the PL peak in the case of CdSe in spite of the different PL peak positions of the pure PS. PL spectra of the PS were examined as function of laser irradiation time and laser intensities.

- N-IV/P9** THE ELECTRONIC STRUCTURE OF ULTRA DISPERSE HYDROXYAPATITES OF CALCIUM AND STRONTIUM, A.P. Shpak, V.L. Karbovskii, L.P. Kluyenko, 36 Vernadsky Str., Institute of Metal Physics, Ukrainian NAS, Kiev 252142, Ukraine

The comparative researches of the electronic structure of compounds Ca₃(PO₄)₂, Ca₁₀(PO₄)₆(OH)₂, Sr₁₀(PO₄)₆(OH)₂, and calcium hydroxyapatite (HAP) of the natural origin (human bone tissue and the bone of Dinosauria Saurolophus lived ~30 mil. years ago) was carried out by XPS, X-ray and NMR- spectroscopy methods. A special feature of the bone-salt HAP is the ultra dispersibility of crystallites. The sizes of bone-salt crystallites do not exceed 50x8x8 nm. We have investigated O K α -, P K β -, Ca K β -, Sr K β -bands, NMR-spectra of P in normal and in ultra disperse conditions. It is ascertained, the characteristic of an electronic spectrum of researched matters essentially varies by transition in a cluster state. The practical correspondence of calcium K-bands in ultra dispersible bone-salt and chemical HAPS, and also significant localization of a calcium d-shell in the inner well of the effective potential are revealed.

The results of this work can be important in the investigation of the processes taking place in the bones after Chernobyl catastrophe, and also in explanation of time-induced changes of bones crystals and in the biomaterials syntheses technology development.

- N-IV/P10** SURFACE ROUGHNESS OF CoSi₂ AND Ba₂SiO₄ BUFFER LAYERS IN YBa₂Cu₃O_{7-x}/BUFFER/Si HETERO-STRUCTURES, I. Belousov, and G. Kuznetsov IMP NAS 252180 Kiev, Ukraine, P. Kus, CU, 84215 Bratislava, Slovakia, S. Linzen and P. Seidel, Institut für Festkörperphysik, FSU Jena, 07743 Jena, Germany

CoSi₂ and Ba₂SiO₄ layers are used as diffusion barriers not only to stabilize the YBa₂Cu₃O_{7-x}/Si structure, but also to design interconnection and electrical insulation elements between a superconductor and a semiconductor. Unfortunately, a film roughness deteriorates YBCO film electrical parameters and complicates its epitaxial growth. It has been demonstrated that reasons for Co/Si reacted layers roughness are local nucleation and lateral crystallization of the silicide phases on crystal defects of the silicon surface. Different methods for the film surface planarization were developed in this work. Co⁺ ion implantation (E=100 keV, D=10¹⁶cm⁻²) into Si surface before the silicidation process allowed us to reduce CoSi₂ layer roughness. The mirror-like ZrO₂/CoSi₂/Si structure was obtained during Co/Si structure silicidation process after deposition of additional Zr thin layers on the top of this structure. Homogeneous and smooth barium silicate films were synthesized onto oxidized Si as opposed to the pure Si surface. The electron beam deposition process for metal films as well as the sintering process were carried out in an ultra-high vacuum system with 10⁻⁷Pa base pressure. Laser ablation and magnetron sputtering methods were used for deposition of YBCO films with transition temperatures T_c = 82-86 K.

- N-IV/P11** EXCIMER LAMP-INDUCED DECOMPOSITION OF PLATINUM ACETYLACETONATE FILMS FOR ELECTROLESS COPPER PLATING, Jun-Ying Zhang and I.W. Boyd, Dept. of E & E Eng., University College London, Torrington Place, London WC1E 7JE, UK

Copper is an attractive interconnect material for use in high density packaging and ultra-large scale integrated (ULSI) devices due to its low resistivity and high electro- and stress-migration resistance. In this paper, photo-induced decomposition platinum acetylacetonate films using an excimer VUV source of 172 nm radiation is presented. VUV irradiation of a substrate coated with platinum acetylacetonate film results in the formation of platinum, which acts as an activator for copper plating by means of a subsequent electroless bath process. Selective copper patterns can thus be formed by employing patterned VUV irradiation. The platinum films formed and the platinum acetylacetonate layers used were characterised using ultraviolet spectrophotometry (UV) and Fourier transform infrared (FTIR) spectroscopy. The morphology of the copper layers was investigated with a scanning electron microscope (SEM). The copper patterns were replicated through a quartz contact mask to dimensions approaching the submicron level. Since larger lamps can in principle be obtained by scaling up the geometry, this large area and low cost VUV-induced metal deposition method could readily available to provide an alternative for the manufacture of thin film microcircuits in ultra-large scale integrated (ULSI) devices.

- N-IV/P12** OXIDATION OF RF PLASMA - HYDROGENATED CRYSTALLINE SILICON, S.Alexandrova and A.Szekeres, Institute of Solid State Physics, Bulgarian Academy of Sciences, Tzarigradsko Chaussee 72, 1784 Sofia, Bulgaria
Use of chemical passivation layers is an important issue in the control of reactive contaminants in future semiconductor manufacturing. Efforts are being made to develop a pre-gate oxide dry cleaning process. The aim of this paper is to present results on the effect of rf plasma hydrogen passivation of Si (100) and (111) on the growth kinetics of thermal SiO₂. Prior oxidation the silicon surface was hydrogenated by exposure to hydrogen plasma in an rf planar unit. The gas pressure was 133 Pa, the input power (13.56 MHz) was 15 W. The substrates were heated up to temperatures of 100°C. The oxidation was performed at 800°C in dry O₂ in accordance with the current tendency in the semiconductor technology. The time intervals are long enough to allow a precise technological control. Silicon dioxide growth data from 5 up to 20 nm for each orientation were carefully examined and compared with those of referent nonhydrogenated wet cleaned Si surfaces. It has been found that the oxidation rates for plasma hydrogenated surfaces are higher in the very thin oxide regime and are not much dependent on the substrate temperature during hydrogenation. As the oxide develops further above ~10 nm, the growth rates slowly approach those of the referent wet cleaned Si surfaces. Discussion on the possible arguments contributing to the enhanced oxidation rates, such as mechanical stress, surface roughness etc., is included.
- N-IV/P13** RESIDUAL STRAIN IN BONDED SOI WAFER AND INFLUENCE ON ELECTRON MOBILITY, T.Jida, T. Itoh, Y. Takano, Science Univ. of Tokyo, 2641 Yamazaki, Noda, 278-0114 Japan
Silicon-on-insulator (SOI) is one of the key technologies for advanced microelectronic devices. In order to realize the reliability and performance on SOI LSI's, structural and electrical characterizations are required on SOI-wafer in detail. In this article, we report residual lattice strain in the bonded SOI layer and its influence to the electron mobility as a function of heat-treatment temperature (900 -1050°C) and duration (6-30 hr.). Bonded n-type SOI layers 1.5 to 5µm thick were measured in this work. Change in residual strain was measured by using X-ray diffraction method. Although the lattice planes between the substrate and the SOI layer are largely tilted each other, we extracted the influences of the tilt successfully and measured the variation of lattice strain in a precise manner. In as-received SOI wafers, expansive strain with order of 10⁻⁵ to 10⁻⁴ was observed. For the specimens annealed at above 950°C, the strain in SOI varied abruptly from expansive to compressive one at annealing time of 12 to 15 hr., then approached a certain value with increasing annealing time. On the other hand, the remaining strain annealed at 900°C exhibited expansive one only, and didn't achieve to compressive one even at long treatment. The variation in lattice strain observed seems to be closely related to the temperature dependent viscoelasticity of SiO₂. Electron mobility was affected considerably with a variation of the residual strain. For 1.5µm thick specimen, although the no strain sample showed identical mobility to a theoretical value, residual strain reduced the mobility down to one half of calculated one. Change in mobility for 5.0µm SOI layers showed smaller than that of 1.5µm. Qualitative analysis was made to understand the formation mechanism of the lattice strain in SOI wafer during heat treatment.
- N-IV/P14** CONFIGURATIONAL MODEL FOR SINGLE-ELECTRON AND PHOTONIC PROCESSES SIMULATION IN NANOSTRUCTURES, A.A.Khodin, Institute of Electronics, National Academy of Sciences, Logoisky tract 22, 220090 Minsk, Belarus
A configurational approach for description of discrete acts of single-electron transport, capture and photonic processes in nanostructures is presented. Active elements sizes of modern solid-state devices, particularly in nano-structures, become much smaller than absorbed or emitted photon wavelength, effective exciton size, etc. Stochastic description of discrete acts of single-electron transport and capture, as well as photonic processes in nanosized regions of porous silicon, aluminium oxide, and so on, cannot be complete. It has been proposed to consider delocalized solitonic single-particle configurations. Two sets of confined configurations corresponding to single electrons and photons are generated by corresponding relativistic limiting condition. In the frames of the approach, electron-electron processes are represented by the relativistic superposition of two electron and intermediate photon configurations and characterized by fine-structure constant. Photon packets are represented by relativistic superposition of corresponding single solitonic configurations. Discrete electron transport features in one-dimensional array of quantum dots having rectangular potential profile and separated by tunnel barriers is analyzed in the frames of the approach.
- N-IV/P15** POROUS ALUMINA AS LOW-E INSULATOR FOR PLANAR SUBMICRON METALLIZATION, S. Lazarouk, P. Jaguiro, S. Katsouba, Belarusian State University Informatics and Electronics, P.Brovki 6, 220027, Minsk, Belarus
Improvements in electronics require increased speed, decreased dimensions. But as dimensions decrease interconnect problems are the most severe limiting factor in IC. Interconnect delay can be minimized by using low-dielectric constant materials for interconnect dielectric. In order to replace SiO₂ with low-ε material based on porous alumina we have developed the technology of in-built aluminum interconnects based on electrochemical Al anodization processes. In our technology aluminum, which is between the interconnect line, is converted in to oxide by using porous electrochemical anodization. Thus we obtain aluminum lines, which are in-built in porous alumina. By using the special regimes of anodization we have obtained the dielectric constant value in the range 3.0 - 4.0. The relief step height for one interconnect level is less than 0.2 µm for 1.0 µm-thick Al films. The process of porous anodization allows to obtain planar surface by using this process for each layer of interconnects and interlevel insulation with in-built contact pillars. The developed processing technique has been tested for CMOS submicron technology.
- N-IV/P16** Si-BASED OPTICAL INTERCONNECTIONS AND THEIR INTEGRATION WITH ELECTRONIC CIRCUIT COMPONENTS, S. Lazarouk, P. Jaguiro, Belarusian State University Informatics and Electronics, P. Brovki 6, 220027, Minsk, Belarus
The prototype of silicon based optical interconnections has been developed and fabricated. The developed design includes reverse biased porous silicon light emitting diodes connected optically by an alumina waveguide. These reverse biased diodes can operate as light emitting diodes at bias voltage more than the avalanche breakdown value and as photodetectors at bias voltages less than the breakdown value. Some parameters of these optoelectronic units have been measured. The developed design can be integrated with electronic circuit components. For example the alumina waveguide can be used as an insulator for planar in-built electronic interconnections. Some other fragments of combined electronic and optical interconnections have been demonstrated. The developed design and technology open new possibilities for integration of electronic and optoelectronic devices.
- N-IV/P17** CONDUCTING AFM STUDIES OF ELECTRON TRANSPORT PROPERTY IN NANOMETER Fe_x(SiO₂)_{1-x} COMPOSITE, W. Wu, J.B. Xu, E.Z. Luo, I.H. Wilson, Dept of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, X. Yan, Department of Physics, Hong Kong University of Science and Technology, Hong Kong
Conventional electrical measurement and microstructure analysis are done separately, it is impossible to study the microstructures and electron transport behaviors simultaneously in nanometer scale. In this paper, we reports the study on mapping the conductive paths in an Fe_x(SiO₂)_{1-x} nano-metal-insulator composite by conducting atomic force microscope (C-AFM), which simultaneously probes local electrical information of buried conducting particles and topography morphology. The local current images and the mean current value as a function of applied bias (I-V) were obtained. It was found that conducting networks were formed at an applied bias of 2 V, through electron transport among the conducting nanoparticles, and the electrons tunneling through the insulating particles has considerable contribution to the conducting network. Information obtained from the C-AFM measurement provided us direct knowledge of the local electrical activity in nanometer scale and identifying metal phase from insulating matrix.

N-IV/P18 DIELECTRIC RELAXATION AND D.C. CONDUCTION PROCESSES IN AMORPHOUS SiO_xN_y THIN FILMS, F. Fernandez Gutierrez*, O. Sanchez Garrido**, M. Hernandez Velez*,*** and J.M. Martinez Duart***, *Facultad de Ciencias ISP " E.J. Varona ", C. de la Habana, Cuba ; **Instituto de Ciencia de Materiales, CSIC, Cantoblanco, 28049 Madrid, Spain ; ***Departamento de Fisica Aplicada, Universidad Autonoma de Madrid, Spain

A study of the d.c. conduction and dielectric relaxation processes in silicon oxynitride thin films deposited by remote-PECVD has been performed. We have measured the capacitance and conductance in the frequency range for 100 Hz to 1 MHz of MIS structures in which silicon oxynitride is the insulator. Using the Kramers - Kronig relations we have obtained the contributions of d.c. conduction and polarization processes. In order to study both processes, phenomenological actual models were applied which allow us to find some relations connecting the activation energies, interfacial trap densities (D_{it}), dielectric parameters and d.c. conductivities. Thus, we have obtained that the D_{it} have great influence on the d.c. conductivity value, although the nature of d.c. conduction is determined by the bulk of the insulator thin film. Another regularity is related to the microstructural order of the films and the height of the interfacial barrier. Finally, most results were also related of the deposition conditions of the films.

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SPL has 15 years of experience in the preparation of crystal surfaces for research and is located in a scientific research centre. SPL uses the latest technology / developments in materials research, therefore enabling it to meet the high standards required for the preparation of single crystal surfaces. Equipment is available for orientation of single crystals using X-ray diffraction, cutting, polishing and characterization of surfaces.

Products

- Metals, Oxides and Alloys single crystals.
- High purity materials (powders, rods, wire, foils, sputter targets, etc.)

Customers of SPL are scientists from USA, Canada, Japan, Australia, China and Europe.

Key products

- Metal single crystals - Oxide single crystals - Alloy single crystals - Materials (high purity) - Polishing - Cutting - Preparation - X-ray diffraction - Powders - Rods - Wire - Foils - Sputter targets.

THOMSON-CSF LASER

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THOMSON-CSF LASER is the new Laser Department of THOMSON-CSF group.

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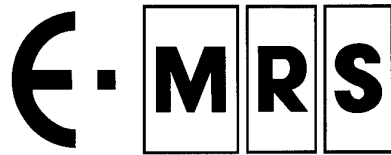
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20:00

**including the presentation of the
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